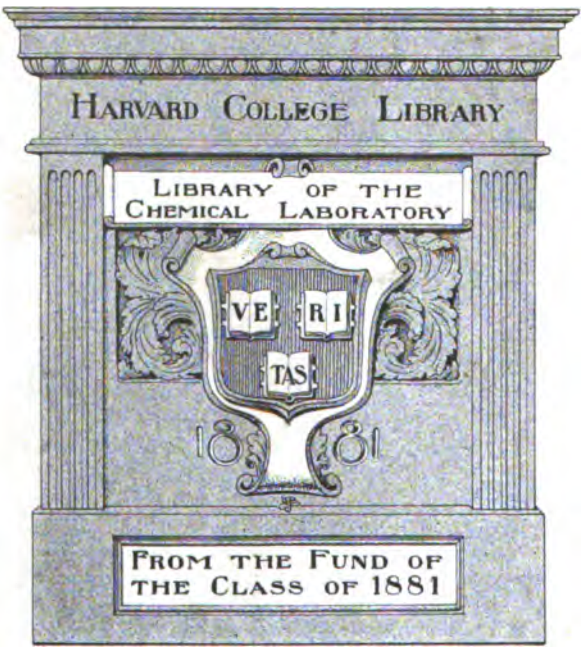

ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

FOURTH EDITION REWRITTEN AND REVISED

EDITED BY HENRY LEFFMANN, M. A., M. D., PROFESSOR OF CHEMISTRY AND TOXICOLOGY IN THE WOMAN'S MEDICAL COLLEGE OF PENNSYLVANIA; W. A. DAVIS, B. Sc., A. C. G. I., FORMERLY LECTURER AND ASSISTANT IN THE CHEMICAL RESEARCH LABORATORY, CITY AND GUILDS COLLEGE, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON; AND SAMUEL S. SADTLER, S. B., VICE-PRESIDENT OF THE AMERICAN ELECTRO-CHEMICAL SOCIETY; MEMBER AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

IN many respects this edition of Allen is a new work. The field of Commercial Organic Analysis has been so enlarged and specialised during the last few years that it has been found necessary to rewrite many parts and add much new matter. Obsolete methods are omitted; what little of the old text remains has been carefully revised and many new illustrations added.

To accomplish the object in view, namely, the furnishing of a modern work of the greatest practical value to the analyst, it was deemed advisable to secure the services of an English and an American editor and to organise a corps of writers particularly versed in the subjects discussed.

The general arrangement of the volumes remains as before, only such changes have been made as will bring the text into line with the latest scientific classification. Great care has been exercised by the editors and contributors in the choice of methods and only those of the highest degree of accuracy and rapidity selected. Effort has been made to secure uniformity in weights and measures, nomenclature and abbreviations. References are to original sources, not to translations or abstracts.

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COMMERCIAL ORGANIC ANALYSIS

VOLUME V

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ALLEN'S COMMERCIAL
ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE ANALYTICAL EXAMINATION OF THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR

THE DETECTION AND ESTIMATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

VOLUME V

Tannins, Analysis of Leather, Dyes and Colouring Matters, Dyestuffs of Groups 6 to 12, Colouring Matters of Natural Origin, Analysis of Colouring Matters, Colouring Matters in Foods, Inks.

BY THE EDITORS AND THE FOLLOWING CONTRIBUTORS

W. P. DREAPER J. F. HEWITT W. M. GARDNER
ALBERT F. SEEKER PERCY H. WALKER E. FEILMANN

FOURTH EDITION. ENTIRELY REWRITTEN

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PREFACE.

The present volume has been completely rewritten, although Dr. Matthews had carefully revised the text as recently as 1906. Dr. Matthews had promised to undertake the revision of a large section of the present volume, but, shortly after commencing, a serious illness unfortunately necessitated his relinquishing the work. Although the text has been largely added to, it will be seen that it still retains the general form given to it by Dr. Matthews. The section on the tannins and leather analysis is in accordance with the best "official" methods of analysis in Europe and the United States and the sections on Inks and Natural Colours have been largely revised and rewritten. The new section on Colouring Matters in Foods should prove useful to Food Analysts and others.

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Albert F. Seeker.

INKS.

Percy H. Walker.

TANNINS.

By W. P. DREAPER, F. I. C.

DESCRIPTION AND GENERAL PROPERTIES OF TANNINS.

Tannic Acids are amorphous or crystalline solids of astringent taste, more or less soluble in water, freely so in alcohol, or a mixture of alcohol and ether, and notably in ethyl acetate. They are almost insoluble in dry ether, and quite so in chloroform, benzene, petroleum spirit, and carbon disulphide. The tannins are generally but little soluble in dilute sulphuric acid. Their aqueous solutions give blue-black or green colourations or precipitates with ferric salts, and are precipitated by the acetates of lead and copper and by stannous chloride. Some tannins are precipitated by tartar emetic and by mineral acids. In some cases tannin combines with the base only, but in others, as when cupric acetate is employed, the salt is said to enter into combination as a whole. With a solution of gelatin, the tannic acids give precipitates, similar to those obtained—with leather, which are insoluble in presence of excess of tannic acid or salts but not wholly insoluble in pure water. The majority of tannic acids can be completely removed from their aqueous solutions by the introduction of rasped skin or hide. The tannic acids are also removed from solution by digestion with cupric or zinc oxide, and they reduce Fehling's solution on heating. A delicate test for tannins is the deep red colour produced on treating a solution with potassium ferricyanide dissolved in ammonia. Tannic acids give insoluble precipitates with many organic bases, the rosaniline and cinchonine compounds being among the least soluble; but it is frequently observable that an alkaloid and a tannin which occur together in the same plant do not combine together to form an insoluble compound.

The most characteristic and commercially useful properties of the tannins are the formation, by combination with gelatin and gelatin-forming tissues, of the insoluble compounds which constitute leather; and the formation of lakes.

The natural tannins are powerful reducing agents, and exhibit a

marked tendency to absorb oxygen, especially in alkaline solution. The oxidation-products are strongly coloured.

Extraction of Tannins.—The different natural tannins exhibit such differences, in their chemical reactions and behaviour with solvents, that it is not possible to give a general rule for their preparation in a state of purity.

The method of Pelouze for the preparation of gallotannic acid from gall-nuts is as follows: The powdered substance is exhausted with ordinary ether containing alcohol and water. On standing, the liquid separates into two layers, the lower of which contains the gallotannic acid while the upper ethereal layer retains the gallic acid. The tannin obtained by separating and evaporating the lower layer may be further purified by dissolving it in water and adding to the solution twice its volume of ether, when three layers are formed, the lowest of which contains nearly pure gallotannic acid. This solution is drawn off, and magnesium sulphate is added to remove the excess of water. The ethereal solution is then evaporated to dryness.

A useful process of extracting tannins is the following: The finely divided substance is exhausted by treatment with rectified spirit, the solution filtered and evaporated to a small bulk at as low a temperature as possible (preferably under reduced pressure). The extract is treated at once with a considerable proportion of cold water, the liquid filtered and fractionally precipitated with lead acetate. The first and last fractions should be rejected, as they usually contain colouring matters and other foreign substances. The tannate of lead is washed as rapidly as possible, suspended in water, and decomposed by hydrogen sulphide. The filtrate is shaken with ether to remove gallic acid, separated from the ethereal layer, and evaporated in a partial vacuum to the consistence of a thin syrup. The remaining water should be removed by exposure over sulphuric acid at the ordinary temperature.

Von Schroeder and Bartel investigated the effect of prolonged boiling in the extraction of tannins. They considered that if sufficient volume of water is used only a few hours of boiling are necessary to extract the largest part of the tannin, succeeding extractions only removing traces of tannin from the residue. Prolonged boiling extracts an excess of non-tannins, therefore it is not advisable to push the extraction, as the quality of the whole product will be deteriorated by the excess of non-tannin constituents.

Parker (*J. Soc. Chem. Ind.*, 1899, **28**, 106) showed that by extracting for a prolonged time at a low temperature, and afterward at a higher temperature, it is possible to fractionate the different tannic acids. Between 60° and 90° seems to be the optimum temperature for the extraction of tannins under ordinary conditions.

Many tannins (*e. g.*, sumac-tannin and ratanhia-tannin) may be purified by agitating with ether to remove gallic acid, saturating the concentrated aqueous solution with common salt, and agitating it with ethyl acetate which then removes the tannin.

Some tannins (*e. g.*, hop- and alder-tannin) are stated to be insoluble in water after isolation, the change being probably due to change in constitution. When the presence of such tannins is suspected, the lead precipitate should be suspended in alcohol instead of water, before decomposing it with hydrogen sulphide.

Many other vegetable substances besides tannins are precipitable by lead acetate, but they are generally insoluble in cold water.

It sometimes happens that a single plant contains two or more tannins. Thus both oak- and willow-bark contain a little gallotannic acid in addition to their own peculiar tannins; myrabolans and divi-divi contain both gallotannic and ellagitannic acids. The existence of several tannins may be detected in some cases by fractional precipitation with lead acetate, and in others by examining the products of the action of dilute acid. Thus, it is stated that oak-red (phlobaphene) produced from quercitannic acid is not removed by agitating the liquid with ether, whilst the gallic acid produced from the gallotannic acid is dissolved in this solvent.

Trimble employed acetone as a solvent, the process being a simple and satisfactory one. The powdered material was generally macerated for 48 hours in a percolator. The solvent was then run off, 500 c.c. being used for each 1,000 grm. of tannin material in a fine state of division. The acetone was removed by evaporation and the residue dissolved in water or alcohol, filtered, and diluted with water until the anhydrides and colouring matters were thrown out of solution.

CLASSIFICATION AND CONSTITUTION OF NATURAL TANNINS.

From the tanner's point of view, the natural tannins are arranged in two general classes, namely, those which produce a "bloom," or fawn-

coloured deposit, on leather, and those which do not. The tannins giving a bloom to leather give a blue-black colouration with ferric acetate, while the others afford a green colour with the same reagent. To the first of these classes belong the tannins of gall-nuts, myrabolans, divi-divi, sumac, valonia, and oak-bark, while the second includes the tannins of catechu, hemlock, larch, ratanhia, mangrove, and all the varieties of mimosa. The production of the "bloom" is in most cases due to the formation of ellagic acid, $C_{14}H_8O_9$, a substance allied to gallic acid, $C_7H_6O_5$, of which most of the tannins of the first group may be derivatives. The tannins of oak-bark and valonia are either mixtures of two distinct tannins or are of unknown constitution, for they yield both gallic acid and protocatechuic acid, $C_7H_6O_4$; while all the tannins which give a green reaction with ferric acetate are probably derivatives of the latter of these acids. These again may be divided into tannins which yield acetic or some other fatty acid on fusion with potassium hydroxide, and those which yield phloroglucinol, $C_6H_6O_3$.

It has been shown by H. Schiff[1] that the ordinary tannin of galls (gallotannic acid) under the influence of dilute acids, or of a peculiar nitrogenous ferment called pectase, splits up into dextrose and gallic acid, thus: $C_{34}H_{28}O_{22} + 4H_2O = C_6H_{12}O_6 + 4C_7H_6O_5$. Many other of the natural tannins also furnish dextrose by the action of dilute acids, but in some cases the change occurs with difficulty. Some of the natural tannins certainly yield no dextrose by the action of dilute acid, and in other cases its formation is still an open question.[2]

The arrangement of natural tannins into classes is therefore based on the products they yield: (1) when heated alone, (2) when heated with dilute acid, and (3) when fused with alkali hydroxide. The characteristic products obtained by heating tannins alone are pyrogallol and catechol; by heating with dilute acids, dextrose, gallic acid, ellagic acid, and insoluble amorphous anhydrides called phlobaphenes; and by fusion with alkali hydroxide, pyrogallol, protocatechuic acid, acetic acid, and phloroglucinol.

In the table on page 7 the principal kinds of tannin are arranged according to the foregoing principles of classification.

[1] Owing to the optical activity of commercial tannin, Schiff suggested a formula by which the substance is represented as containing an asymmetric carbon atom. Walden's experiments (*Ber.* 1897, 30, 3151), however, show that commercial tannin is not only a mixture, but also varies in composition, and therefore, its optical behavior cannot be used in a theory regarding its structure.

[2] Valonia is liable to a natural fermentation (ropiness), in which a large quantity of dextrin, or some similar substance precipitated by alcohol, is formed.

Certain of the tannins give a blue or black colouration when mixed in solution with ferric salts, while others yield a green or greenish colour when similarly treated. Speaking generally, the tannins which are derived from gallic acid give a blue indication, while those derived from protocatechuic acid afford a green colour.

The behaviour with iron salts is best observed by adding to an aqueous solution of the tannin contained in a test-tube one or two drops of a dilute solution of ferric acetate. This may be prepared by adding sodium acetate to a solution of ferric chloride. Excess of the reagent must be carefully avoided, or its colour and oxidising action may lead to error. The colouration produced by ferric acetate having been observed, it is advisable to add an excess of ammonia, and note any change which may occur.

If ferric chloride be substituted for the acetate, the general results are the same, but in some instances a greenish colouration is produced by tannins which give a distinct blue colour with ferric acetate. This is especially the case if the ferric chloride solution contains free acid. Hence the acetate is to be preferred as a reagent for tannins. Other reactions of tannins are given on pages 42 and 43.

Prescott[1] gave the following comparative table of the different kinds of tannins:

(1) Glucoside-tannins, when boiled with dilute mineral acids yield (*a*) a crystallisable acid or its anhydride, or (*b*) a phlobaphene and a reducing sugar.	(1) Tannins not glucosides.
(2) Iron-blueing tannins with ferric salts give blue to black precipitates or colours. The ferroso-ferric solutions, slightly basic, give the best reactions. Mineral acids dissolve and destroy colour.	(2) Iron-greening tannins,[2] with basic ferric salts, give greenish precipitates or colours. Brown colours sometimes obtained.
(3) Tannins, not tanning agents, do not form leather, nor preserve animal membrane, though they precipitate solutions of gelatin.	(3) Tanning materials change animal membrane into leather, not putrescible. Also precipitate solutions of gelatin.
(4) Tannins which on being sublimed, or on being fused with potassium hydroxide, yield a trihydroxyphenol, such as pyrogallol, $C_6H_3(OH)_3$.	(4) Tannins which in subliming yield a dihydroxyphenol, $C_6H_4(OH)_2$, and on fusion with potassium hydroxide yield an acid as protocatechuic acid, $C_6H_3(OH)_2CO_2H$.
(5) Pathological tannins. Found in punctured vegetable tissue. Gallo-tannins, including sumac-tannins.	(5) Physiological tannins, from uninjured vegetable tissues include various glucosides and iron-blueing tannins.

[1] Organic Analysis, 1895.
[2] Of this class only willow-tannin is a glucoside.

The Stanhouse-Procter classification of tannins is as follows:

Group I. Tannins which give a blueish colour with ferric chloride yield when treated with alkali hydroxides, pyrogallol, and form on the surface of the tanned skin the so-called "bloom" (ellagic acid).

Group II. Tannins which give a green colour with ferric chloride, with bromine water marked precipitates, and yield with alkali hydroxides pyrocatechol derivatives which form the so-called reds (phlobaphenes).

Group III. A small group which gives with ferric chloride a blueish-green colour, and with bromine water an ill-defined precipitate, yielding little "phlobaphenes," but a marked "bloom."

Distinction Between Alcoholic and Aqueous Tannins.—This distinction is of importance, as in some countries a duty is only collected on alcoholic tannin. A tannin which has been prepared by extraction with water, on treatment with ether and a subsequent evaporation of the ethereal extract, leaves a residue which, redissolved in alcohol, does not precipitate on the addition of water. On the contrary, a tannin which has been prepared by extraction with alcohol, gives under the same conditions a distinct precipitate, due to the fats and resins which accompany it.

The following is a description of the best methods of formation and recognition of the decomposition-products obtained by the action of heat, dilute acids, and fused potassium hydroxide on different kinds of tannin.

General Behaviour of Tannins: Action of Heat.—When a tannin which produces a "bloom" on leather is cautiously heated to about 200°, it is decomposed with volatilisation of pyrogallol in feathery crystals. On the other hand, the tannins which produce no bloom, but red deposits, show a somewhat similar behaviour, but the sublimate consists of catechol. From oak-bark and valonia, which apparently contain a mixture of both kinds of tannin, and hence yield both bloom and red colouring matters, both catechol and pyrogallol are produced on heating.

In using the heating test for distinguishing the two classes of tannins, the temperature must be carefully regulated, or further changes take place and the recognition of the pyrogallol or catechol will be complicated by the formation of metagallic acid and other secondary products. A better result is obtained by mixing the substance with several times its weight of sand or powdered pumice, and passing a stream of coal-

Tannin	Source	Composition	Products on heating with dilute acid	Products of dry distillation	Products on fusion with potassium hydroxide	Reaction with ferric acetate	Remarks
Digallic acid	Gall-nuts	$C_{14}H_{10}O_9$	Gallic acid only	Pyrogallol	Pyrogallol and carbonate.	Blue-black.	
Gallotannic acid (Glucoside).	Gall-nuts	$C_{34}H_{28}O_{22}$	Gallic acid and dextrose.	Pyrogallic and metagallic acids.	Pyrogallol and carbonate acid.	Blue-black.	
Ellagitannic acid	Divi-divi; myrabolams.	$C_{14}H_{10}O_{10}$	Ellagic acid only.	Pyrogallol	....	Nearly black	
Sumac-tannin	Sumac leaves	$C_{16}H_{14}O_{10}$	Gallic acid	Do.	....	Blue-black	Possibly identical with gallotannic acid.
Pomegranate-tannin	Pomegranate rind.	....	Ellagic acid and dextrose.	Do.	....	Blue-black.	
Caffetannic acid	Coffee berries	$C_{14}H_{16}O_7$	Caffeic acid and dextrose.	Catechol	Protocatechuic and acetic acids.	Green.	
Cinchotannic acid	Cinchona-bark	$C_{14}H_{16}O_9$	China red and dextrose.	Do.	Do.	Green	Very soluble in ether, etc.; two varieties exist.
Fern-tannin	Male-fern	....	Filix-red and dextrose.	Do.	Do.		
Maté-tannin	Paraguay tea	....	?and dextrose.				
Valonia-tannin	Valonia	....	Valonia red	Catechol and pyrogallol.	Protocatechuic and gallic acids.	Blue-black.	
Quercitannic acid	Oak-bark; tea-leaves.	$C_{19}H_{16}O_{10}$	Oak-red	Do.	Protocatechuic acid and phloroglucinol.	Blue-black.	
Ulmotannic acid	Elm-bark	....	Elm-red	Do.	Do.	Dirty green	Probably identical with oak-tannin.
Salitannic acid	Willow-bark	....	Phlobaphene	Catechol	Do.	Deep black.	
Lingué-tannin	*Laurus caustica*	$C_{17}H_{17}O_9$	Phlobaphene	Do.	Do.	Green.	
Hemlock-tannin	Hemlock	$C_{20}H_{18}O_{10}$	Hemlock-red	Do.	Do.	Green.	
Catechu-tannic acid	Catechu	$C_{38}H_{34}O_{15}$	Catechin	Do.	Do.	Greenish.	
Kinotannic acid	Kino	$C_{28}H_{21}O_{11}$	Kino-red	Catechol and phenol.	Do.	Green.	Alcoholic solution gelatinises.
Ratanhia-tannin	Ratanhia	....	Ratanhia-red	....	Do.	Green	Does not precipitate tartar-emetic.
Chestnut-tannin	Horse-chestnut	$C_{26}H_{24}O_{12}$	Chestnut-red	....	Do.	Green	Does not precipitate tar-tar-emetic.
Morintannic acid	Fustic	$C_{13}H_{10}O_6$	Rufimoric acid	Catechol	Do.	Greenish	Crystallisable: yellow.
Tormentil-tannin	Tormentilla	....	Tormentil-red	....	Do.	Green.	
Quebrachitannic acid	*Quebracho lorentsii.*	....	Quebracho-red	Catechol	Do.	Green.	Precipitates gelatin and albumin.
Alder-tannin	Alder-bark.	$C_{27}H_{28}O_{11}$	Alder-red and dextrose.	Do. Do.	Pholoroglucinol and protocatechuic and acetic acids.	Dirty green.	Insoluble in water after extraction. Does not ppt. tartar-emetic.
Lupulo-tannic acid	Hops.	$C_{25}H_{24}O_{13}$	Hop-red and dextrose.	Do.	Do.	Greenish.	
Animal tannin	Corn weevils.	$C_{28}H_{16}O_{16}$	....	....	....	Blue-black	

gas or carbon dioxide through the retort, so as to carry the products quickly out of the sphere of action. A still better and more convenient plan is the following, based on an observation of T. E. Thorpe (*Chem. News*, 1881, **43**, 109): About 1 grm. of the sample should be heated with 3 c.c. of pure glycerin to a temperature of 190° to 200° for 20 minutes. After cooling, the product is treated with about 20 c.c. of water, and the liquid shaken with an equal volume of ether without previous filtration. The ethereal layer, which contains the pyrogallol and catechol, is separated from the aqueous liquid, evaporated to dryness, and the residue dissolved in 50 c.c. of warm water. The filtered solution is divided into several portions which are respectively tested with lime-water, ferric chloride, and ferric acetate. These reagents readily distinguish catechol from pyrogallol in the absence of the other, and will suffice for the recognition of the one in presence of not too large a proportion of the second substance. It must be remembered that the production of pyrogallol may have resulted from the presence of gallic acid in the original substance, if the tannin had not previously been purified therefrom in the manner indicated on page 2. Catechol, on the other hand, may be a product of the decomposition of catechin and other substances allied to and associated with tannins, unless care has been taken to remove them previously. As a general rule, however, catechins and catechol-derivatives only occur in quantity with catechol tannins, and the same is true of gallic acid with regard to pyrogallol.

The Stiasny test may also be applied to ascertain the presence or absence of catechol tannins. It is applied as follows:

50 c.c. of the solution is boiled for 10 minutes with 10 c.c. of 40% formaldehyde and 10 c.c. hydrochloric acid. (1 : 1) and then cooled and filtered. If the filtrate is tested with 1 or 2 drops of gelatine-salt solution, and 1 c.c. ferric alum (1%) solution with the addition of 5 grm. sodium acetate, catechol tannins are completely precipitated by this reagent, pyrogallol tannins giving a blue or violet layer at the junction with the ferric salt. 5% myrabolan extract can be detected in quebracho or mimosa extract in this way.

Only catechol tannins form diazo-compounds with diazo-benzene-chloride. This process may be used for estimating the catechol tannins in sumach, the nitrogen being estimated in the precipitate. (Nierenstein and Webster, *Collegium*, 1907, **262**, 224).

Insoluble bromine derivatives are formed from dilute solutions of

the catechol tannins by the addition of bromine water. They also generally show a crimson colour with concentrated sulphuric acid, the pyrogallic tannins giving yellow or brown shades.

A. Seyda (*Chem. Zeit.*, 1898, **22**, 1085) describes a delicate test for tannins. He has noticed that if gold chloride is added to a very dilute solution of tannin a clear purple liquid is obtained. The principal use of this test is to determine the presence of tannin in highly coloured extracts. Before applying the test they are diluted until practically colourless, the gold chloride is added, and the liquid allowed to stand for half an hour.

The characters of catechol have already been described (Vol. III.).

Action of Dilute Acids on Tannins. Phlobaphenes.

As already stated, many tannins are resolved on heating with dilute acids into dextrose, and either gallic acid, ellagic acid, or an amorphous, insoluble red colouring matter or phlobaphene, according to the nature of the tannin. Other tannins yield these products without dextrose being simultaneously formed. As a rule, the action of dilute acid on a tannin results in the formation, apart from dextrose, of a single decomposition-product belonging to the aromatic series (*e. g.*, gallic acid, ellagic acid, phlobaphene, etc.), but in some cases two or more of such substances are obtained from a tannin of apparently homogeneous nature (page 3).

To ascertain whether a tannin yields dextrose by hydrolysis, it may be freed from any admixture of carbohydrates by precipitation with neutral lead acetate, or saturation of the aqueous solution with salt and removal of the tannin by agitation with ethyl acetate in the manner indicated on page 3. The washed lead salt, or the tannin left on evaporating the ethyl acetate solution, is then heated to 100° for some hours, with dilute hydrochloric acid, in a sealed tube or firmly closed bottle. (Mere boiling with the dilute acid, replacing loss by evaporation, is sufficient in most cases, especially for qualitative purposes.) After cooling and opening the vessel, the mixture should be allowed to stand for some time in the cold, to observe whether any sparingly soluble product separates.[1] In such case, the precipitate should be filtered off, and any traces remaining in solution removed by agitating

[1] To prevent subsequent error, it is desirable to get rid of any gallic acid, by repeatedly agitating the solution of the tannin with ether before precipitating with lead acetate.

the filtrate first with ethyl acetate and then with ordinary ether. The aqueous liquid is boiled, neutralised with sodium carbonate, precipitated with basic lead acetate (to remove any traces of tannin or colouring matters), the liquid again filtered, the excess of lead removed by dilute sulphuric acid, the filtered liquid again neutralised by sodium carbonate, and heated to the b. p. with Fehling's solution, when a yellow or red precipitate of cuprous oxide will prove the presence of dextrose. This latter may also be indicated by a fermentation test with yeast, or by an optical examination as to rotatory power.

The *precipitate* obtained on cooling the product of the action of dilute acid on the tannin may consist of lead chloride (if the lead compound has been used), ellagic acid, or a phlobaphene. The lead chloride may be removed by washing with boiling water. If the residue has a pale yellow or fawn colour, and is but slightly soluble in cold alcohol, it probably consists of ellagic acid, which is soluble in ammonia and hot alcohol, and dissolves readily in strong nitric acid giving an intense crimson colouration. A red-coloured residue, readily soluble in cold alcohol, will consist of a phlobaphene, which will be reprecipitated on diluting the alcoholic solution with water, and may be further examined by fusion with potassium hydroxide.

The *ethereal layer*, obtained by shaking the filtrate from the ellagic acid and phlobaphenes with ether and ethyl acetate, will contain gallic acid, if any has been formed in the treatment of the tannin with dilute acid. For its recognition the ethereal solution should be evaporated to dryness, the residue treated with cold water, and the solution filtered. The filtrate will give a fine red colour with potassium cyanide, if gallic acid has been produced. The test may be confirmed by treating another portion of the filtrate with an aqueous solution of picric acid, followed by ammonia, when a reddish colour, changing to a fine green, will be produced if gallic acid be present.

It is sometimes sufficient to boil the tannin or its infusion with dilute hydrochloric acid for some time, replacing the acid lost by evaporation. The solution is then diluted and allowed to cool, when ellagic acid and phlobaphenes will separate, and may be filtered off and separated by treatment with cold alcohol as already indicated.

Phlobaphenes.—The phlobaphenes are anhydrides of the respective tannic acids from which they are derived, being formed from these tannins by the loss of one or more molecules of water. They are produced by the action of dilute acids on tannins. They may also be

formed in many cases by pouring alcoholic or highly concentrated aqueous solutions of the tannins into cold water, under which circumstances a part of the tannin becomes insoluble and the phlobaphene separates as a red precipitate. Phlobaphenes exist ready-formed in most tannin materials capable of producing them, and may be dissolved out of these or their dried extracts by means of alcohol.

The phlobaphenes are red or brown amorphous substances, difficultly soluble in water, weak acid solutions, or in pure ether, but soluble in water containing ammonia, and freely soluble in alcohol. Some phlobaphenes are so sparingly soluble in water, even when boiling, that this characteristic may be utilised for the estimation of the corresponding tannin. This is especially the case if, after heating with hydrochloric acid, the liquid be evaporated to dryness and the residue treated with water. The decomposition-products often remain almost entirely insoluble, for, though generally insoluble in pure water, they are dissolved more or less by solutions of sugar and other substances. The phlobaphenes are also dissolved by dilute alkalies and alkali carbonates, and by borax, which last substance is said to be used in the preparation of some tannin extracts, and has been suggested as a means of rendering phlobaphenes available for tanning. The solubility of the phlobaphenes in water seems to depend on their degree of hydration, many tannins giving a whole series of anhydrides, of which those containing one molecule of water less than the original tannin are soluble in water, while the higher members of the series become less and less soluble as they lose the elements of water. The soluble phlobaphenes are the colouring matters of tanning materials, and behave like the tannins themselves, precipitating gelatin and combining with hide to form leather.[1]

The phlobaphenes somewhat resemble the resins in their properties, as, for example, their solubility in alcohol and slight solubility in water, and their behaviour when fused with alkali hydroxides; but they are distinguished from the resins by dissolving in dilute ammonia. With gelatin, ferric acetate, and lead acetate the phlobaphenes usually behave like their respective tannic acids. Occasionally a so-called tannin is met with (*e. g.*, hop-tannin), which is not precipitated by gelatin, while the phlobaphene produced therefrom is precipitated.

[1] Hemlock-bark yields a series of such substances, of which the lower members are deep-red soluble tannins, and the higher form the red sediment which occurs in hemlock extract. It is not possible to decolourise hemlock extract without at the same time greatly reducing its tanning powers, though by preparing and concentrating it at a low temperature the proportion of insoluble higher anhydrides formed may be kept at a minimum.

Phlobaphenes are yielded by the tannic acids from the bark of the oak, elm, horse-chestnut, willow, birch, fir, and acacia, as well as by the tannins from rhubarb, male-fern, wine, etc. According to Grabowski, the phlobaphenes from the tannins of the oak, ratanhia, and tormentilla are not merely analogous to but actually identical with chestnut-red (see Quercitannic Acid).

Action of Fused Alkali on Tannins. Phloroglucinol.

When tannins are subjected to the action of alkali hydroxide in a state of incipient fusion, they are decomposed with formation of products varying with their constitution. Tannins yielding catechol on dry distillation, that is, all those which give a green colour with ferric acetate—and valonia and oak-bark tannins in addition—give protocatechuic acid when fused with potassium hydroxide. On the other hand, those tannins which give pyrogallol when heated alone yield gallic or ellagic acid when fused with alkali hydroxides.[1] In each case the action brings about the elimination of CO_2.

The tannins which yield protocatechuic acid on fusion with alkali hydroxides may be further subdivided according to the secondary product formed simultaneously, one class giving acetic or some other fatty acid, and a second class, phloroglucinol (page 13).[2] A third class, including the tannins of the alder and hop, give both acetic acid and phloroglucinol, but this peculiarity is not improbably due to the coexistence of 2 distinct tannins.[3] All those tannins which yield acetic acid instead of phloroglucinol on fusion with potassium hydroxide give notable proportions of dextrose on heating with dilute acid, while some, and probably all, of the phloroglucinol tannins give no sensible quantity of dextrose.

To recognise the presence of a phloroglucinol-tannin without employing the tedious method described below, H. R. Procter mixes 5 c.c. of water, 1 c.c. of a saturated solution of commercial aniline

[1] The relationship of these products of the decomposition of tannins may be indicated by the following formulæ:

$$\underset{\text{(Dihydroxybenzoic acid)}}{\text{Protocatechuic acid}}\ C_6H_3\begin{cases}OH(^1)\\OH(^2)\\H\\CO.OH(^4)\end{cases} - CO_2 = \underset{\text{(Pyrocatechin)}}{\text{Catechol}}\ C_6H_3\begin{cases}OH(^1)\\OH(^2)\\H\\H\end{cases}$$

$$\underset{\text{(Trihydroxybenzoic acid)}}{\text{Gallic acid}}\ C_6H_2\begin{cases}OH\\OH\\OH\\CO.OH\end{cases} - CO_2 = \underset{\text{(Pyrogallic acid)}}{\text{Pyrogallol}}\ C_6H_2\begin{cases}OH(^1)\\OH(^2)\\OH(^3)\\H\end{cases}$$

[2] The formation of these products is due to a change allied to saponification, thus:

$$\underset{\text{Morintannic Acid.}}{C_{13}H_{10}O_6} + KHO = \underset{\text{Potassium Protocatechuate.}}{KC_7H_5O_4} + \underset{\text{Phloroglucinol.}}{C_6H_6O_3}.$$

[3] The fusion of gallic acid with sodium hydroxide is said to result in the formation of a small quantity of phloroglucinol (*J. Chem. Soc.*, 1883, 44, 60).

nitrate, and 1 c.c. of a very dilute solution of potassium nitrite. To this liquid is added 1 c.c. of a solution containing as nearly as possible 0.5 per cent. of the tannin to be examined. If phloroglucinol or phloroglucinol-tannin be present the liquid will gradually become yellow or orange, and will deposit a cinnabar-red precipitate after standing for a time not exceeding 1 hour, but many other substances also give precipitates under these conditions. Thus the indication is produced by oak-bark infusion, which is not supposed to contain a phloroglucinol-tannin, and gall-tannin, pyrogallol, and other substances give similar but browner precipitates. A sharper distinction may be obtained by employing dilute solutions, but it is advisable also, whenever possible, to act on the tannin with fusing potassium hydroxide and examine the products.

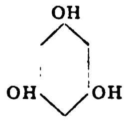
The fusion with potassium hydroxide may be conducted on the original tannin, or on the substance produced by treating it with dilute acid. The lead salt may be substituted for the free tannic acid. The separation or recognition of protocatechuic and gallic acids or pyrogallol when mixed is troublesome, and hence it is more satisfactory in most cases to aim at the isolation and recognition of phloroglucinol. The following method may be followed: 20 grm. of the tannin, phlobaphene, or lead salt are boiled with 150 c.c. of solution of potassium hydroxide, of 1.2 sp. gr. for 2 or 3 hours, and the liquid then concentrated, stirring continually till it becomes pasty, the mixture then undergoing fusion.[1] The product is cooled, and treated with dilute sulphuric acid in quantity sufficient to render the whole distinctly acid when cold, the liquid is filtered from the potassium sulphate and other solid matters, and the filtrate is treated with sodium hydrogen carbonate till its wine-red colouration with litmus (or absence of red colouration with methyl-orange) shows that the sulphuric acid is neutralised. The liquid is then shaken several times with ether, and the ethereal solution evaporated. The residue contains phloroglucinol, recognisable by its sweet taste and reactions with ferric chloride and pine-wood. If necessary, it may be purified from protocatechuic acid by precipitating the aqueous solution with neutral lead acetate, the filtrate being extracted with ether, or evaporated after separating the excess of lead by hydrogen sulphide.

Phloroglucinol. Phloroglucin. $C_6H_6O_3$.—This substance is

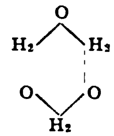
[1] In some cases, such as that of phloretin, it is sufficient to boil the substance with potassium hydroxide solution, as described in the text, omitting the subsequent evaporation and fusion.

isomeric with pyrogallol and hydroxyquinol. As it possesses both hydroxylic and ketonic properties. It is probable that it exists in two isodynamic forms, one of which is readily converted into the other.[1]

[1] Sym-trihydroxybenzene.



Isodynamic form (triketohexamethylene.)



Phloroglucinol forms small plates or rhombic tablets containing $2H_2O$. It becomes anhydrous at 100°, and melts at 218° if heated rapidly, but at 209° or even 200° if slowly heated. At a higher temperature it sublimes without odour, and solidifies again on cooling.

Phloroglucinol is sweeter than cane-sugar. It is soluble in water and alcohol, and readily in ether, and by agitation with the last solvent can be removed from its aqueous solution. An aqueous solution of phloroglucinol is not precipitated by any metallic salt except basic lead acetate. It is coloured deep violet by ferric chloride, and reduces Fehling's solution and ammonio-nitrate of silver. In concentrated aqueous solution it is converted by bromine into tribromophloroglucinol, $C_6H_3Br_3O_3$, which immediately separates in long needles, the liquid emitting a powerful, and tear-exciting odour.

When dilute solutions of phloroglucinol and nitrate of toluidine or aniline are mixed, and a very dilute solution of potassium nitrite added, the liquid gradually becomes turbid and of a brownish-yellow colour, then orange-red, and finally a vermilion-red precipitate is produced. The test is a delicate one.

If a freshly-cut slip of deal wood be moistened with a dilute solution of phloroglucinol (0.5%), and subsequently with dilute hydrochloric acid, it acquires an intense violet or red colour. The reaction is also a delicate one.[1]

Action of Other Reagents or Tannin.—By heating a mixture of tannin, potassium hydrogen sulphate and ethyl acetoacetate at 190°–200°, two different compounds are obtained: 1. Ditannacetoacetic ester, $C_{34}H_{32}O_{22}$, a yellowish-grey powder which is slightly soluble in cold water and decomposed by hot water; soluble in alcohol and acetic ether. 2. Tannacetoacetic ester, $C_{20}H_{20}O_{12}$, which is scarcely soluble

[1] The colour is readily obtained with infusion of gambier and probably of other phloroglucinol tannins, but is also given by catechol.

in either cold or hot water, readily soluble in alcohol, ether, and ethyl acetoacetate. By the action of glycerine on a mixture of tannin and potassium hydrogen sulphate substances are produced which, according to their empirical formula, are reduced anhydro-derivatives of tannin or gallic acid, with properties similar to hydroquercitannic and hydroquergallic acids, the reduction products of the oak-bark tannic acids. From the mixture so obtained have been isolated: 1. Hydrotannic acid $C_{14}H_{14}O_7$, possessing the properties of tannin, but with stronger reducing power. It is a brown powder, soluble in ammonia, alcohol, and dilute acetic acid, but insoluble in water. 2. Isohydrotannic acid, $C_{14}H_{14}O_7 \cdot H_2O$, a brown powder, soluble in ammonia and dilute boiling alcohol, and slightly so in hot water, but insoluble in cold water.

If tannin is heated with glycerine or dextrose, a compound is formed which is readily soluble in water and dilute acetic acid. The tannin glyceride is obtained as a colourless or slightly brownish-coloured syrup, while the glucoside is a solid substance which forms a syrup with water.

P. Sisley (*Rev. gen. des. Mat. Col.*, 1897, **16**, 219) gives a résumé of the effect of various agents on tannin substances. Tannin solutions when exposed to the air absorb oxygen and become brown in colour. A series of oxidation products is obtained, acid in character, and rendering tannin solutions unfit for mordanting in light shades. This oxidation does not seem to be dependent upon fermentation, and takes place more rapidly in dilute than in concentrated extracts. The presence of acid retards the change, whereas alkalies accelerate it in consequence of the phenolic character of tannin. Reducing agents bring about a decolourisation of dilute tannin solutions, which, however, is not permanent, the reducing agent itself becoming oxidised. The protosalts of metals which are capable of different degrees of oxidation and which act as oxygen carriers behave similarly. With concentrated extracts sulphurous acid is useful and preserves them comparatively well, but with diluted extracts the sulphurous acid is oxidised too rapidly. Arsenious and phosphorous acids, however, give satisfactory results when used in small quantities.

Dilute acids appear to hydrolyse tannins at high temperatures with the formation of gallic acid.

Solutions of tannins contain usually varying quantities of nitrogenous and pectic substances, glucosides, and mineral constituents,

and these facilitate the growth of ferments. This fermentation may convert the tannin into gallic acid; further action then taking place, and carbonic, butyric, oxalic, and lactic acids being formed. The glucosides present also undergo alcoholic fermentation and give rise to the wine-like odour to be noticed in fermented extracts.

Gallotannic Acid. Digallic Acid. Tannic Acid. Tannin.

Gallotannic acid occurs in gall-nuts in proportions commonly ranging from 60 to 77%, and is usually prepared therefrom by the method of Pelouze described on page 2.[1]

Another plan is to extract gall-nuts with a mixture of 12 parts of ether and 3 of alcohol, 12 parts of water being added to the extract, and the alcohol and ether removed by distillation. The residual aqueous solution is then filtered and evaporated, the product being further purified by solution in water and treatment with animal charcoal. To obtain the tannin in a spongy form, the syrupy solution should be mixed with alcohol and ether and evaporated at a moderate temperature. The spongy form dissolves very readily.

Pure gallotannic acid may also be obtained, according to Schiff, by extracting gall-nuts with anhydrous ether to which 5% of alcohol has been added.

As prepared by Pelouze's process, tannin yields more or less dextrose or an analogous substance when treated with dilute acids (the amount obtained varying from 0 to 22%), gallic acid being formed at the same time. Ordinary tannin has been represented by the empirical formula $C_{34}H_{28}O_{22}$, which would yield 23% of dextrose on hydrolysis. As prepared by Schiff's process, however, gallotannic acid yields little or no dextrose on treatment with dilute acid, though agreeing in its other characters with the product obtained by Pelouze's method.

H. Schiff obtained a gallotannic acid synthetically by taking gallic acid dried at 110°, mixing it into a thin paste with phosphorus oxychloride, and heating the mixture first to 100° and then at 120°. Hydrogen chloride is evolved, and the gallic acid is converted into a yellow powder, which should be washed with ether and dissolved in water. The unchanged gallic acid is allowed to crystallise out, after which the solution is saturated with common salt, the precipitated tannin is washed with brine and redissolved in ether alcohol. The product thus

[1] A further purification may be effected by fractionally precipitating the aqueous solution of the product by acetate of lead, the first and last fractions being rejected. The lead tannate is then treated with a quantity of solution of oxalic acid insufficient for its complete decomposition, and the liquid filtered and evaporated, *in vacuo*

obtained gives all the reactions of purified gall-tannin, but is perfectly reconverted into gallic acid on boiling with hydrochloric acid, without the formation of any trace of dextrose or ellagic acid.

It has been generally considered that pure gallotannic acid or tannin from galls has the composition $C_{14}H_{10}O_9$, and in constitution is the anhydride of gallic acid, or *digallic acid.*[1] It is still suggested in certain quarters that tannic acid is a glucoside. Feist as recently as 1908 has suggested a formula, $C_{27}H_{22}O_{17}$, based on the assumption. Nierenstein and Sisley hold the opposite view, contending that those investigators who still consider that tannic acid is a glucoside, have not removed all the tannic and gallic acids from the solution before examining its reducing power with Fehling's solution.

The following facts tend to elucidate the constitution of gallotannic acid:

1. The formation of gallic acid by hydrolysis from tannic acid: $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$.

2. The formation of gallamide and ammonium gallate in almost theoretical proportions by boiling gallotannic acid with aqueous ammonia in an atmosphere of hydrogen:

$$\begin{aligned} & C_6H_2\ (OH)_3.CO.O.C_6H_2\ (OH)_2.CO_2H + 2NH_3 \\ & = C_6H_2\ (OH)_3.CO.NH_2 + C_6H_2\ (OH)_3.CO_2.NH_4. \end{aligned}$$

3. The formation of a pent-acetyl-derivative by boiling tannin with acetic anhydride for 1 hour, the 5 hydroxyl groups being replaced by a corresponding number of acetoxyl groups.

4. The formation of tannin, or a substance giving all its reactions, by heating monobromoprotocatechuic acid with potassium gallate and alcohol: $C_6H_2\ (OH)_3.COOK + BrC_6H_2(OH)_2.COOH = KBr + C_6H_2\ (OH)_3.CO.O.C_6H_2(OH)_2.COOH$.

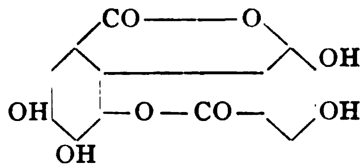
Recent investigations by Nierenstein (*Ber.*, 1908, **41**, 3015; 1908, **42**, 1122, 1910, **43**, 628 and 1910, **44**, 1267) have brought to light certain reactions which agree with the following formula for tannic acid (tannin).

$$\mathrm{HO.C}{\Large\langle}\begin{array}{l}\mathrm{C(OH).CH}\\ \mathrm{C(OH){:}CH}\end{array}{\Large\rangle}\mathrm{C.CO.OC}{\Large\langle}\begin{array}{l}\mathrm{C(OH).COH}\\ \mathrm{CH{:}C(CO_2H)}\end{array}{\Large\rangle}\mathrm{CH.}$$

[1] P. Walden (*Ber.*, 1899, 32, 3167) has shown that the molecular weight of tannin is two to four times that of digallic acid. Spectroscopic investigation of tannin and digallic acid also shows that their absorptive powers for all regions of the spectrum are entirely different, the extinction coefficient of tannin being always considerably lower than that of digallic acid.

Recently Iljin (*Ber.*, 1909, 42, 1731) gives the rotatory power of the pure acid free from ash as +76.5°. He does not confirm its composition as that of digallic acid.

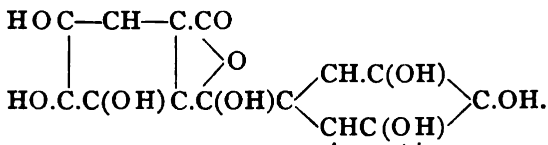
When boiled with hydrogen peroxide, tannin yields ellagic acid of which the constitutional formula is said by this authority to be



and penta-hydroxydiphenylmethylolide carboxylic acid

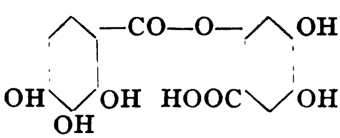
$$\begin{array}{l} \quad\; C_6H(OH)_3.CO \\ \quad\;\;\; | \qquad\qquad\;\; | \\ CO_2H.C_6H(OH)_2.O \end{array}$$

which occurs in reddish brown needles darkening at 305° and decomposing at 338°–342° and gives a reddish brown colour with $NaHCO_3$ and a yellow one with concentrated sulphuric acid. Gallic acid heated with As_2O_3 gives Schiff's α-digallic acid, and categallic acid is obtained from protocatechuic acid. When tannin is esterified (Werner's method) a gallic acid methyl ester is formed. This does not indicate a ketonic formula for tannin, nor does it entirely support the digallic formula. Dekker's formula

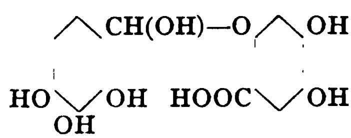


Asymmetric.

is not considered by Nierenstein to be supported by the fact that he could only prepare the acetyl derivative $C_{14}H_6O_9Ac_5$, for this formula requires seven acetyl groups. He regards tannic acid as a mixture of at least two compounds represented by the following formulæ:



Digallic acid.



Leucotannic acid.

Hydrates of an ethyl ester of gallotannic acid have been isolated by Manning. (*J. Amer. Chem. Soc.*, 1910, **32**, 1312.) They have also been prepared from glucose and ethyl gallate. One of them has the

formula $C_{41}H_{27}O_{21}(OC_2H_5)_5 . 5H_2O$. This supports the formula $C_{41}H_{32}O_{26}$, for gallotannic acid. Feist has suggested that tannin from Turkey gall nuts, consists of a glycogallic acid as a base to which two molecules of gallic acid are attached in the nature of an ester. (*Co.*, 1910, 219.)

Glueckmann, (*Collegium*, 1907, 269, etc.) considers that if the compounds formed with alkalis are phenylates and not salts that the acid value for tannin should be nil. He considers that tannic acid must be a monobasic acid ($C_{14}H_{10}O_9$) and that probably the group causing tanning will be found to be the *phenolic hydroxyl* one.

The nature of these tannins and the closely allied natural colouring matters have been investigated by Perkin in a series of papers published in the *J. Chem. Soc.* in 1896, 1897, and 1898 and also by Kostanecki (*Ber.*, 1895, **26**, 2091, etc.) but the more theoretical text-books must be consulted for particulars of these investigations.

"Pure" gallotannic acid forms a colourless amorphous mass, light yellowish buff-coloured scales, or a brittle vitreous mass. It becomes yellow in the light even if air be excluded. The taste is strongly astringent, and the reaction acid. When heated it darkens with or without fusing, and at 215° decomposes with volatilisation of water, pyrogallol, and carbon dioxide, while a residue of metagallic or melanogallic acid, $C_6H_4O_2$, is left. This last substance is the sole product when tannin is rapidly heated to 280°. It is a black, amorphous, tasteless substance. The optical activity of gallotannic acid is said by Rosenheim and Schidrowitz (*Trans.*, 1898, 73, 878) to show a value $(\alpha)_D = 75°$ to $75.2°$.

Gallotannic acid is soluble in 6 parts of cold water, and more readily in hot. It is precipitated from its concentrated solution by dilute hydrochloric or sulphuric acid, common salt, and potassium chloride and acetate, but not by sodium sulphate or nitric acid. Skin and other gelatinous tissues remove it completely from its aqueous solution. When the solutions are dilute, saline matter must be present to cause precipitation.

In absolute alcohol gallotannic acid dissolves sparingly, but it is more soluble in alcohol containing water. In absolutely dry ether free from alcohol, tannin is almost insoluble; after a certain portion of water has been added the liquid separates into three layers. When 100 grm. of tannin are treated with 150 c.c. of ether, and 100 c.c. of water added, the lowest layer is a concentrated aqueous solution of tannin; the middle

layer contains some tannin and much water; while the uppermost layer consists of ether holding a little tannic acid in solution.

Gallotannic acid is practically insoluble in chloroform, benzene, petroleum ether, and carbon disulphide. In ethyl acetate and in glycerine it is readily soluble.

When taken internally gallotannic acid is converted into gallic acid, which may afterward be found in the blood and urine. Tannin diffuses but slowly in aqueous solution, but may be dialysed from its solution in alcohol. It is known that gallotannic acid is present in a simple form in alcohol, but in a state of molecular aggregation in aqueous solution.

Gallotannic acid is readily oxidisable. It reduces the salts of gold, silver, mercury, and copper, permanganates, etc. Nitric acid rapidly oxidises it, with formation of oxalic acid; and chlorine, bromine, iodine, and chromic acid act readily on this substance.

Gallotannic acid decomposes carbonates and acts as a monobasic acid. Its solution in alkali hydroxides rapidly oxidises, and acquires a brown colour. The gallotannates are amorphous and difficult to prepare in a pure state. Most of them are insoluble.

One of the most important and characteristic reactions of gallotannic acid is the formation of a white (or buff-coloured) flocculent precipitate with a solution of gelatin. This coagulum, which is the basis of leather, is not completely insoluble in pure water, but is wholly insoluble in presence of excess of tannic acid. When freshly formed it is often extremely finely divided, and passes through the closest filter, but coagulates on adding ammonium chloride, alum, and certain other neutral salts.

Added to a dilute solution of gallotannic acid, ferrous sulphate occasions no change, if free from ferric salt, but produces a white precipitate in a concentrated solution. With ferric chloride tannin produces a bluish-black precipitate of ferric gallotannate (ink), the colour of which is destroyed by boiling, or reducing agents. Addition of hydrochloric acid in excess dissolves the precipitate, which is reproduced on adding sodium acetate. Ferric acetate behaves like ferric chloride.

Gallotannic acid gives no reaction with a solution of cupric sulphate, but on adding excess of ammonia, or in the presence of calcium carbonate, is completely precipitated. The reaction may be employed for its estimation. Fehling's solution is reduced by gallotannic acid on heating.

With tartar emetic, and soluble salts of lead and bismuth, gallotannic yields white insoluble precipitates. With lime-water and with ammoniacal barium chloride it yields a white precipitate, turning blue on exposure.

Gallotannic acid is not precipitated by calcium acetate from a solution slightly acidified with acetic acid, and the solution remains clear even after adding twice its volume of alcohol (separation from tartrates, citrates, oxalates, malates, etc.).

With an ammoniacal solution of potassium ferricyanide, gallotannic acid produces a deep red colour changing to brown, even in very dilute solutions. The test, which was first observed by Allen, is very delicate, but the colour is destroyed by a large excess of the reagent. A somewhat similar behaviour is shown by gallic acid.[1]

Ammonium molybdate yields with tannin a red colouration, which is yellow in dilute solutions, and is destroyed on adding oxalic acid.

Gallotannic acid may be estimated with considerable accuracy by oxidation with a standard solution of permanganate (page 22).

Gallotannic acid may be extracted from its acidified aqueous solutions by repeatedly agitating with ethyl acetate free from alcohol, and may thus be separated from tartaric, citric, malic, and other vegetable acids, but not from gallic acid.

Some of these reactions furnish important distinctions between gallotannic acid and gallic acid and pyrogallol, which in many respects it closely resembles. The table on page 51 shows the reactions of gallotannic and gallic acids and pyrogallol. The comparative reactions of gallotannic acid and other tannins are given on page 7.

Commercial gallotannic acid is often very impure. It may contain more or less dextrose, chlorophyll, volatile oil, gallic and ellagic acids. Starch has been found to the extent of 25%.

Dextrose may be detected by precipitating the solution of the sample with basic acetate of lead, and heating the filtrate with Fehling's solution. A *glucoside* may be detected by the same method, after boiling the solution with dilute sulphuric acid for ten minutes, and neutralising the solution with alkali.[2]

[1] G. Griggi gives the following reaction. Gallic acid in dilute solution gives a bright ruby-red colour with potassium cyanide, which disappears on standing, but is reformed on agitating in presence of air or by the addition of hydrogen peroxide. A solution of tannin or pyrogallol gives a yellowish-red colour with potassium cyanide, which is more slowly decolourised. The addition of excess of hydrogen peroxide gives a permanent yellow-brown colour with gallic acid and a dirty white precipitate with tannin.

[2] According to J. E. Saul (*Pharm J.*, [3] 1887, 17, 387), a very delicate test for dextrose, by which it can usually be detected in samples of commercial tannin, is to agitate about 0.01 grm. of the sample with 3 c.c. water, and then add 3 drops of an alcoholic solution of

If *chlorophyll* be present, on shaking the sample with an equal weight of water and the same volume of ether, the ethereal layer will be coloured more or less greenish.

Gallotannic acid should be entirely soluble in alcohol. If a residue be left it should be examined for *starch*.

Mineral adulterants will be indicated by ignition. Commercial tannin leaves a very insignificant proportion of ash, 0.4% being apparently the maximum proportion recorded.

Gallic acid may be detected in commercial tannin by separating the tannin by the special lead solution (see page 78) and then testing the the filtrate with ferric chloride. Oengummed silk absorbs both tannic and gallic acids, but according to Vignon, tannin is much more readily absorbed than gallic acid.

A method which is said to be capable of detecting traces of gallic acid in tannin has been described by S. Young (*Chem. News*, 1883, **48**, 31). The sample is dissolved in a little water, ether added equal in volume to about 1/3 of the water used, and the whole well shaken. On standing, 3 layers are formed. The ethereal or uppermost is removed, evaporated, and the residue dissolved in water and tested with potassium cyanide, when a strong red colouration will be obtained if the sample contained even a trace of gallic acid. The middle layer contains still more gallic acid, while the lowest aqueous layer is almost free from it. By repeating the agitation with ether several times a more complete separation of the gallic acid can be effected.

A determination of the actual *gallotannic acid* present in the commercial article may be made by Löwenthal's permanganate method, or by the hide powder or copper process. The residue of "not tannin" does not appear always to consist entirely of gallic acid, dextrose being probably present in some cases. The following results were obtained by T. Maben (*Pharm. Journ.*, [3], 1885, **15**, 852), by applying Löwenthal's method to representative specimens of commercial tannin. The *moisture* was estimated by drying the samples *in vacuo* over sulphuric acid.[1]

thymol. 3 c.c. of concentrated sulphuric acid should then be poured in so as to form a separate layer below the aqueous liquid. Under these circumstances, tannin containing sugar yields a turbid deep rose-coloured solution, gallic acid remains untinted, or merely develops a very faint pink tint in the sulphuric acid layer; and pyrogallol yields a dull violet solution.

[1] According to C. Böttinger (*Annalen*, 1888, **246**, 124), even the purest commercial tannin is not a uniform substance. When heated to 150°, under pressure, with concentrated hydrochloric acid, it gives off a gas burning with a green-edged flame (methyl chloride; and on heating the tannin with water and excess of bromine, small quantities of products

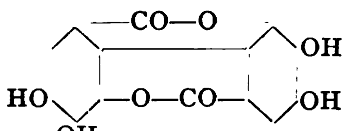
	1	2	3	4	5	6	7	8	9
Moisture......................	5.0	8.0	5.0	7.0	6.0	7.0	3.0	3.0	4.0
Gallotannic acid...............	88.8	86.9	54.4	56.9	79.9	77.3	82.3	59.7	70.7
Not-tannin (by difference)......	6.2	5.1	40.6	36.1	14.1	15.8	14.3	37.3	25.3
$KMnO_4$ required for "not tannin,"	5.86	1.92	6.01	6.94	1.08	3.08	6.63	5.55	3.89

Ellagitannic Acid. $C_{14}H_{10}O_{10}$.

This variety of tannin is contained in divi-divi and myrabolan, and as a glucoside in pomegranate rind. When boiled with dilute acids or heated with water to 110° in a sealed tube, it loses water and yields the anhydride, ellagic acid. In its other chemical behaviour, ellagitannic closely resembles gallotannic acid, but gives a light brown precipitate with cupric acetate.

Ellagic Acid.

$C_{14}H_6O_8$, or

possibly 

(Nierenstein.)

This acid is formed when a concentrated aqueous solution of gallotannic acid is exposed for a considerable time to the air, or by its reaction with iodine: $C_{14}H_{10}O_9 + I_2 = 2HI + C_{14}H_8O_9$. Ellagic acid is also produced by the dehydration of ellagitannic acid (see above), and by the action of oxidising agents on gallic acid. It is said to be a constituent of bezoar stones.[1] Air-dried ellagic acid contains 1 molecule of water, which it loses at 100° and re-absorbs in moist air. When heated to 200° it loses H_2O, and forms an anhydride, $C_{14}H_6O_8$, which is slowly reconverted into ellagic acid by boiling with water (compare, however, Nierenstein's recent work, *loc. cit.*). When pure, ellagic acid forms a sulphur-yellow crystalline substance, nearly insoluble in

volatile with steam are produced. Nevertheless such tannin is almost completely fixed by hide, and yields nothing but gallic acid when boiled with aqueous alkali hydroxides. When boiled with a mixture of phenylhydrazine hydrochloride and sodium acetate it becomes intensely yellow, changing to a brownish-yellow coagulated mass on standing. This reaction is said not to take place in the presence of a sugar.

[1] Ellagic acid is readily prepared by pouring a concentrated alcoholic extract of divi-divi into water. The precipitate may be purified by crystallisation from hot alcohol. It may also be obtained by boiling the aqueous extracts of divi-divi, myrabolans, pomegranate rind, etc., with dilute hydrochloric acid, and may be purified by solution in alcohol. It may also be prepared by heating gallic acid with dry arsenic acid to 160° but the product is difficult to purify from arsenic. It may be obtained from bezoa- stones (intestinal concretions of a Persian species of goat) by boiling with potassium hydroxide and precipitating with hydrochloric acid.

water, even at 100°, and but slightly soluble in alcohol. The aqueous and alcoholic solutions have an acid reaction. It is but slightly soluble in ether, but small quantities may be effectually extracted from the aqueous solution by agitation with that solvent. In potassium hydroxide ellagic acid dissolves to a yellow solution which rapidly becomes darker, and black crystals of potassium glaucomelanate separate. Neutral ferric chloride, when shaken with solid ellagic acid, is coloured greenish at first, but afterward becomes inky black. The solution of ellagic acid in hot alcohol has a pale yellow colour, and deposits the acid in sulphur-yellow crystals on cooling. With lead acetate ellagic acid yields a precipitate containing 63% of PbO. Ellagic acid dissolves in fuming nitric acid with deep crimson colouration. With the product from divi-divi, the nitric acid solution retains its crimson colour on dilution with water, but when derived from other sources, dilution is said to change the colour to orange.

Nierenstein (*Collegium*, 1910, 265) gives further results of investigations dealing with the formula and constitution of ellagic acid.

Caffetannic Acid. Caffetannin. $C_{14}H_{16}O_7$.

This variety of tannic acid occurs in coffee berries. When isolated it forms a brittle mass or a yellowish-white powder. It is only slightly soluble in ether. On boiling caffetannic acid with dilute sulphuric acid, or by exposing its solution in alkali hydroxide to the air, the liquid acquires a bluish-green colour owing to the formation of the oxidation-product, viridic acid. This substance is characterised by giving a blue precipitate with lead acetate and a crimson colour with strong sulphuric acid. On prolonged boiling with alkali hydroxides, caffetannic acid yields caffeic acid, $C_9H_8O_4$, which crystallises from the neutralised solutions. When fused with potassium hydroxide, caffetannic acid yields protocatechuic and acetic acids. Heated alone, it gives catechol. Ferric chloride gives a dark green colour with caffetannic acid, and cinchonine sulphate a white precipitate, but solution of gelatin is not affected.

Quercitannic Acid. Quercitannin.[1]

According to C. Etti (*J. Chem. Soc.*, 1883, **44**, 994) the tannin of oak-bark exists in two forms, namely, as quercitannic acid, and as an anhydride of that acid, or phlobaphene.[2]

1 Quercitannic acid is said to be identical with the tannins of the elm, willow, and black tea.

2 Quercitannic acid may be prepared from treating oak-bark with alcohol, evaporating

Quercitannic acid is not a glucoside, the reactions which formerly caused confusion being really due to the presence of lævulin, which on treating the oak-bark with dilute sulphuric acid was converted into lævulose.[1]

Quercitannic acid is amorphous, brownish-red, and readily soluble in water and alcohol. When pure, it dissolves completely in ethyl acetate, but not in pure ether or benzene.

In very dilute alcoholic solution, quercitannic acid yields a pure yellow precipitate with neutral or basic acetate of lead, but in aqueous solution the precipitate produced is light brown. With ferric salts quercitannic acid gives a blue-black colour, and yellowish-white precipitates with tartar-emetic, gelatin, albumin, and alkaloids. It is also precipitated by solution of lead nitrate, ammoniacal chlorides of zinc and magnesium, ammoniacal sulphate and acetate of copper, and by molybdate of ammonium. It readily reduces permanganate and Fehling's solution. According to Procter, a dilute solution of quercitannic acid does not precipitate blood-albumin, but renders it uncoagulable by heat, even in presence of free acid.

According to Etti, quercitannic acid has the composition $C_{17}H_{16}O_9$.[2] At 130° to 140° it gives up water and yields the first anhydride or phlobaphene, $C_{34}H_{30}O_{17}$, which is brownish-red, nearly insoluble in water and in ether, but readily soluble in alcohol or mixtures of the same with water. It exists in the original bark together with quercitannic acid and gives a brownish-red precipitate with lead acetate. When boiled with dilute sulphuric or hydrochloric acid, the phlobaphene loses 1 molecule of water and yields a second anhydride, $C_{34}H_{28}O_{16}$, from which a third, $C_{34}H_{26}O_{15}$, may be obtained. All these anhydrydes are soluble in alcohol and alkali hydroxides, and are precipi-

the filtered liquid, dissolving the extract in water, and agitating the solution with ethyl acetate. The product obtained on separating and evaporating the ethereal layer is accompanied by a brownish-green terpene resin and with some of the anhydrides of the tannin. The resin may be removed by treating the dried extract with ether or benzene, in which it is readily soluble; and the phlobaphenes or tannin-anhydrides may be separated by dissolving the tannin in ether-alcohol, or partially by mere solution in cold water. Or the soluble anhydrides may be precipitated by saturating the aqueous solution of the alcoholic extract with common salt before shaking with acetic ether.

[1] Tannic acids, which are almost insoluble in water, do not seemingly occur in combination with a sugar, and are therefore not glucosides; their basis is said to be a ketone acid and is formed from 2 molecules of gallic acid with the elimination of 1 molecule of water.

[2] Etti points out the following distinctions between gallotannic and quercitannic acids:

	Gallotannic Acid.	*Quercitannic Acid.*
Heated with dilute sulphuric acid to 140° under pressure,	Yields gallic acid, giving a white precipitate with lead acetate.	Yields phlobaphene or oak-red, giving a brown precipitate with lead acetate.
Heated with acetic anhydride,	Forms aceto-tannins.	Yields anhydrides and acetylised anhydrides.
Boiled with aqueous ammonia in an atmosphere of hydrogen,	Yields gallamide and ammonium gallate.	Yields indefinite resinous products.

tated blue-black by ferric chloride. Löwe has obtained a fourth anhydride, $C_{34}H_{24}O_{14}$, which he designates oak-bark red, a name which has been applied by other observers to the first and second anhydrides.

Tanners class the anhydrides as "colouring matter," and reject barks cr extracts containing a large proportion, as they impart too red a colour to the leather, as in the case of red mangrove.

From the number and mode of formation of these anhydrides, together with the evolution of methyl chloride on heating the tannin under pressure with dilute hydrochloric acid, Etti concludes that quercitannic acid is a methyl-derivative of digallic, or gallyl-gallic acid. Etti also investigated a tannic acid of the formula $C_{20}H_{20}O_9$, obtained from the bark of a different species of oak. This agreed with the other acid in all its properties, except that it gave a bluish-green colour with ferric chloride, rapidly changing to deep green, and on addition of sodium carbonate first to blue and then to red. This variety of tannin yields four anhydrides similar in character to those of the acid with 17 atoms of carbon.

Löwe (*J. Chem. Soc.*, 1881, **40**, 901) gives $C_{28}H_{26}O_{15}$ as the formula of the hydrated tannic acid of oak-bark, and $C_{28}H_{22}O_{11}$ as that of the oak-red. Böttinger (*Ber.*, 1883, **16**, 2710) adduces evidence in favour of $C_{19}H_{16}O_{10}$ as the formula of the tannic acid, and $C_{38}H_{26}O_{17}$ as that of the oak-red. He has also attributed to the latter the formula $(C_{14}H_{10}O_6)_2H_2O$. To the tannin of oak-*wood* he attributes the formula $C_{15}H_{12}O_9$.[1] Etti gave the formula of the tannin of *Q. pubescens* as $C_{24}H_{20}O_9$, which agrees fairly well with Trimble's ultimate analysis results: C=59.79, H=5.08, O=35.13.

According to Etti, most of the sparingly soluble ketone tannic acids occur in plants in combination with a metallic base, probably magnesium. By concentrating the aqueous extract, precipitating with

1 It is possible that the varying statements respecting the composition of oak-bark tannin are due to the presence of 2 analogous substances. According to F. Musset (*Dingl. Polyt., J.*, 253, 8, 340), this is actually the case, both tannins being precipited by gelatin and oxidised by permanganate. One, which he terms oak-tannin, may be extracted by repeatedly agitating the infusion with acetic ether, in which the oak-red tannin is insoluble. He prefers, however, to estimate the oak-red tannin by precipitation with iodine, avoiding presence of air. The compound formed contains 7.8% of iodine and an equal quantity of iodine is converted into hydriodic acid. An equal quantity of the infusion is treated with zinc oxide, and, after twenty-four hours, and the absence of more than traces of tannin in the filtered solution being proved by gelatin and ferric acetate, the non-tannin matters are titrated with a N/10 solution of iodine. By deducting the amount of iodine required by the non-tannin matters from that consumed by an equal measure of the original infusion the iodine which has reacted with the tannins is found, and by subtracting from this twice the quantity of iodine contained in the precipitate of iodine oak-red tannin, the iodine corresponding to the oak tannin is ascertained. Examined in this manner, Musset found German oak-barks to contain from 7 to 8% of oak-tannin, and 6 to 10% of oak-red tannin.

hydrochloric acid, and purifying the resulting tannic acid by extracting with alcohol and ether, he claims to have succeeded in isolating acids of the following composition:

$C_{16}H_{14}O_9$ from the stalk oak,
$C_{18}H_{18}O_9$ from tannery oak-bark,
$C_{20}H_{22}O$ from copper beech-bark,
$C_{22}H_{26}O_9$ from hop-cones.

That the first acid contains a ketone group is shown by the formation of a phenylhydrazine derivative and an oxime.

Tannin from Animal Sources.

A substance having the character of a tannin has been extracted from corn weevils. 3% was obtained of a substance forming small reddish-yellow scales soluble in water, alcohol, aqueous ether, etc., and precipitating gelatin, albumin, and alkaloids. It gave a blueish-black colouration with ferric salts, and on boiling with dilute sulphuric acid split up into dextrose, gallic acid, and a red phlobaphene.

Lupulotannic Acid. Hop-tannin. $C_{24}H_{24}O_{13}$.

The tannin of hops is a glucoside which is easily soluble in water and proof spirit, but not in ether. It gives a green colour with ferric salts, a dirty green precipitate with cupric sulphate, a yellow with lead acetate, and a brownish-yellow precipitate with lime-water. It reduces Fehling's solution. Lupulotannic acid yields a precipitate with albumin but not with gelatin, unless it be previously dried at 100°, by which treatment it is converted into the anhydride or phlobaphene, $C_{50}H_{46}O_{25}$, a substance coexisting with lupulotannic acid in the hop, and having all the characteristics of a tannin. According to Etti, it is a glucoside which yields protocatechuic acid, phlorogucinol, and dextrose. It precipitates gelatin solution completely, and reduces Fehling's solution. It is soluble in alcohol and in alkalies, and is precipitated on acidifying the latter solution.

Catechu-tannic Acid. Mimotannic Acid. $C_{15}H_{14}O_6$.

The tannins which yield catechol when heated differ from the pyrogallol derivatives by giving a green colouration with ferric acetate. Like oak-bark tannin, they give insoluble red phlobaphenes or anhy-

drides by the action of dilute acids. Their constitution is in most cases imperfectly understood. The tannin of catechu is typical of this class of tannic acids.

Catechu-tannic acid, probably identical with the substance described as mimotannic acid, is the astringent substance contained in catechu (cutch) and gambier.[1] It is extracted by cold water from catechu, and is also formed by heating catechin alone to 130°, with water to 110°, or by boiling it with alkali hydroxides. Catechu-tannic acid is a dark reddish-brown powder, moderately soluble in water, insoluble in ether, but readily soluble in alcohol and in ethyl acetate. It resembles gallotannic acid in many of its characters, but gives a greyish-green precipitate with ferric salts, and no reaction with ferrous salts. It is also distinguished from gallotannic acid by giving a dense precipitate with cupric sulphate and none with tartar-emetic; and by yielding catechol and phloroglucol by fusion with potassium hydroxide. The aqueous solution is precipitated by gelatin, albumin, and dilute sulphuric acid. When treated with hydrochloric acid and potassium chlorate in excess, catechu-tannic acid yields a chlorinated-substitution-product which is turned purple-red by sodium sulphite. Catechin gives the same reaction.

Catechins.

Catechu and gambier contain from 20 to 30% of a substance called catechin, which appears to be the type of a number of similar substances occurring in all or most tannin materials yielding catechol-tannins. A catechin has been recognized in Colorado quebracho, and the kinoin of kino is of similar nature. The co-existence of several homologous or closely analogous substances of the nature of catechin, even in catechu itself, is the probable explanation of the difference in the formula assigned to catechin by different observers. Unless qualified in some way, by the term catechin the substance contained in catechu (cutch) or gambier is understood.

Catechin may be prepared from gambier or catechu by digesting the powdered substance in cold water to remove the catechu-tannic acid, and exhausting the residue with boiling water. Impure catechin deposits as the solution cools, and may be redissolved in boiling water and decolourised by animal charcoal.

[1] It is doubtful whether the tannin of gambier is identical with that of catechu.

Catechin forms a white powder consisting of silky crystalline needles. It melts at 217° and yields a sublimate of catechol on further heating. It dissolves readily in alcohol and boiling water, but requires 1133 parts of cold water for solution. Agitation with ethers or ethyl acetate extracts it from its aqueous solution, a fact which may be utilized for its purification. Though sometimes called catechuic acid, catechin possesses no acid properties, though it is soluble in alkalies. The alkaline solution turns brown on exposure to air. Catechin dissolves in strong sulphuric acid with deep purple colouration. The aqueous solution gives white precipitates with lead acetate and mercuric chloride, and reduces ammonio-nitrate of silver, but, unlike the tannins, does not precipitate gelatin, alkaloids, or tartar-emetic; on the other hand, it gives a precipitate with albumin. It is oxidised by permanganate in presence of free acid, a fact which may be utilised for its estimation (page 60). Heated under pressure to 140° with dilute sulphuric acid, catechin yields catechol and phloroglucinol. With diazobenzene chloride, catechin gives a red crystalline precipitate, which is soluble in alcohol and ether, and dyes wool golden-brown.

Catechin has been described as an anhydride of mimotannic acid, the tannin of catechu and gambier, but according to Etti the opposite of this is probably the case. In constitution, catechin is possibly a phloroglucide. This view accounts for its decomposition by fusing alkali hydroxide with evolution of hydrogen and formation of protocatechuic acid and phloroglucinol: $C_6H_7.COOH : 2C_6H_3(OH)_2 + 4H(OH) = C_6H_3(OH)_2.COOH + 2C_6H_3(OH)_3 + 2H_2$.

Different observers, however, are not agreed as to the composition of catechin. Thus Liebermann and Tauchert, who prepared a crystallised diacetyl-derivative, attribute to catechin from catechu the formula $C_{21}H_{20}O_9 + 5H_2O$ (*Ber.*, 1880, **13**, 694).

By the graduated action of heat or dilute acid on catechin it is said to be successively converted into the following anhydrides:

Catechin, .	$2C_{19}H_{18}O_8 = C_{38}H_{36}O_{16}$	Not acid; does not precipitate gelatin.
Catechin-red; Catechu-tannic acid, . . .	$C_{38}H_{34}O_{15}$	Acid; precipitates gelatin.
Di-anhydride, . . .	$C_{38}H_{32}O_{14}$	
Tri-anhydride, . . .	$C_{38}H_{30}O_{13}$	Insoluble in water.
Catechuretin,	$2C_{19}H_{14}O_6 = C_{38}H_{28}O_{12}$	

Gautier isolated 3 catechins from gambier. Kostanecki and Tambor (*Ber.*, 1902, **35**, 1867 and *ibid.*, 2410) may be consulted for further details. Catechol, phloroglucinol, and a red anhydride are produced when heated at 140° with 1 : 8 sulphuric acid.

Kinoin, $C_{14}H_{12}O_6$, a substance resembling catechin, is obtained from green or Malabar kino by boiling with dilute hydrochloric acid, decanting from the precipitated kino-red, and agitating with ether. When recrystallised from hot water it forms small colourless prisms, which are difficultly soluble in cold water but readily in hot water and in alcohol. Its solution is coloured red by ferric chloride. Heated at 120°–130° it yields the anhydride, kino-red, $C_{28}H_{22}O_{11}$, and this when heated at 160°–170° gives $C_{28}H_{20}O_{10}$. Both anhydrides are precipitated by gelatin, but kinoïn itself is not. When heated with hydrochloric acid at 120°–130°, kinoïn yields methyl chloride, gallic acid, and catechol, and hence probably has the constitution of a guaiacol or methyl-catechol gallate.

According to Hennig kino-red is a colouring matter in intimate combination with a tannic acid supposedly identical with gall-tannin. As it possesses acid properties, kino-red has been termed *kinoic-acid.*

Kino is quite extensively employed in medicine, as it is a powerful astringent, for the purpose of suppressing morbid discharges.

Tannin-yielding Materials.

The following table gives the common names of the principal tannin-yielding substances used in commerce, together with the botanical names of the plants producing them, the parts of the plant used, and the usual percentage of tannin said to be contained in good specimens of each material:

Common name of material	Botanical name of plant	Part of plant used	Ordinary % of tannin
Oak-bark	Quercus pedunculata and Q. robur.	Bark	8–13
Cork-bark	Quercus suber	Inner bark	10–14
Valonia	Quercus ægilops	Acorn-cups	25–35
Chestnut-oak extract.	Quercus (an American species)	Extract from bark.	20–25
Hemlock-bark	Abies Canadensis	Bark	10–14
Hemlock-extract	Abies Canadensis	Extract from bark.	18–28
Churco-bark	Oxalis gigantea (Chili) ?	Bark	26
Monesia-bark	Chrysophyllum glycyphlœum	Bark	32
Mangrove-bark	Rhizophora mangla	Bark	9–33
Alder-bark	Alnus glutinosa	Bark	16
Larch-bark	Abies larix	Bark	6–8
Mimosa (Wattle)	Acacia dealbata and A. molissima.	Bark	24–30
Catechu (Cutch)	Acacia and Areca catechu	Extract from wood.	45–55
Gambier	Uncaria gambir and U. acida	Extract from leaves and small branches.	36–40
Sumac	Rhus coriaria, R. cotinus, etc	Leaves	15–30
Chestnut-wood	Castanea vera	Wood	8–10
Chestnut-extract	Do.	Extract from wood.	14–20
Quebracho-wood	Aspidosperum quebracho, etc.	Wood	14–23
Quebracho-extract, solid.	Do.	Extract from wood.	53–60
Quebracho-extract, liquid.	Do.	Do. do.	36
Marsh Rosemary	Statice coriaria	Root	20–24
Ratanhia	Krameria triandria	Root	38–42
Myrabolans	Terminalia chebula and T. belerica.	Fruit	20–40
Divi-divi	Cæsalpina coriaria	Pod	30–50
Kino	Pterocarpus marsupium, and Drepanocarpus senegalensis	Extract from fruit.	75
Gall-nuts	Quercus infectoria, etc.	Galls	60–77
Tamarisk galls	Tamarix Indica, and T. Africana.	Galls	50–54
Rove	? (Greece and Asia Minor)	Galls	24–34

C. Councler (*Dingl. Polyt. J.*, 1885, **253**, 483) has published the following results. The method of analysis was probably von Schroeder's modification of Löwenthal's process.

	Moisture	Tannin	
		Total	Readily soluble
Mimosa-bark, Tasmania	11.35	16.88	15.05
Mimosa-bark, Tasmania	8.25	23.12	19.93
Mimosa-bark, Victoria	11.75	21.20	16.54
Mimosa-bark, Victoria	9.25	17.30	12.70
Boot-bark of Kermes Oak, "Garouille" (*Quercus coccifera*).	10.00	8.69	7.88
Birch-bark, Friedrichsruh		4.97	3.98
Alder-bark, Riesenthal	18.00	11.68	11.15
Alder-bark, Riesenthal	10.70	7.38	5.35
Alder-bark, Riesenthal	6.80	8.17	6.02
Alder-bark, Riesenthal	10.50	12.53	11.82
Alder-bark, Riesenthal	11.67	11.15	8.93
Willow-bark, Russian, *Salix purpurea*	7.8	1.72	0.86
Willow-bark, Russian, *viminalis*	7.9	3.42	2.14
Willow-bark, Russian, *purpurea*	8.7	4.71	2.70
Willow-bark, Russian, *capsica*	13.4	2.62	1.34
Willow-bark, Russian, *amygdalina*	7.6	3.17	2.27
Quebracho-wood (highest)	11.3	19.36	10.97
Quebracho-wood (lowest)	10.0	16.42	7.66
Chestnut-wood	7.3	8.49	5.48

The following results by Kay and Bastow (*J.S.D. and C.*, 1887, 3, 132) were obtained by the assay of tanning materials exhibited in the Indian and Colonial Exhibition of 1886. The process employed was Procter's modification of Löwenthal's method (see page 60).

Tanning material	Percentage of tannin	
	In terms of oxalic acid	In terms of gallotannic acid
Terminalia tomentosa (galls)	9.24	6.53
Terminalia belerica (fruit)	12.86	8.48
Terminalia chebula (fruit)	52.65	34.49
Ceriops Rosburghiana (bark)	37.65	24.66
Camia auriculata	19.94	12.86
Acacia catechu (extract)	76.00	....
Acacia catechu (bark)	21.35	....
Acacia arabica (pods)	22.44	....
Areca catechu (nuts)	14.28	....

F. Simand (*Gerber*, 1883, 211) gives the following results of the assay of various tannin extracts by the Löwenthal-Neubauer method.

Extract from	Density, Baumé	Tannin		Remarks
		Total	Soluble in cold water	
Quebracho-wood, solid	....	73.08	70.09	Dried before analysis.
Valonia, solid	....	70.44	68.59	Do.
Oak-wood, liquid	13°	14.47	15.09	Do.
Ooak-bark, liquid	32°	24.37	23.72	Commercial extract.
Fir, liquid	32°	14.31	13.72	Do.
Chestnut-wood, liquid	31°	23.52	22.68	Do.
Sumac, liquid	34°	13.38	10.75	Do.

I. Ishikama has published the following figures showing the strength, in terms of gallotannic acid, of various tannin-yielding materials of Japanese origin (*Chem. News*, 1880, **42**, 274).

	Percentage of tannin (in terms of gallotannic acid).
Gall-nuts (Japanese)	58.8 to 67.7
Gall-nuts (Chinese)	77.4
Fruit of *Alnus firma*	25.3 to 27.5
Bark of *Myrica rubra*	10.5 to 15.0
Rind of Pomegranate	20.4
Betel-nut	18.0
Oak-bark (*Quercus dentata*) (inner)	7.4
Oak-bark (*Quercus dentata*) (outer)	2 6

D. Hooper (*Amer. J. Pharm.*, 1894, 377) has examined a large number of Indian tannin-yielding plants for the amount of tannin which they contain. The following table gives a summary of his results:

	% tannin		% tannin
Bridelia montaria	39.4	Mangifera indica	16.7
Acacia pycriantha	33.8	Eugenia arnottiana	16.1
Acacia decurrens	33.4	Terminalia arjunn	16.0
Terminalia chebula	31.0	Anogeissus latifolia	15.5
Psidium Guejava	27.4	Dioxpyrus embryopteris	15.0
Candelia Rheedii	27.4	Saxifraga ligulata	14.2
Acacia Melarioxylon	26.8	Ficus racemosa	14.1
Acacia leucophloea	20.8	Myrica nogi	13.7
Woodfortia floribunda	20.6	Cassia fistula	12.9
Acacia arabica	25.5	Diospyrus (fruit)	12.4
Cassia auriculata	20.7	Eugenia Jarubal	12.4
Rhodomytrus tomentosa	19.5	Eugenia Jarubolana	12.0
Macaranga Ronburgi	18.4	Eugenia montana	11.9
Casuarina equisetifolia	18.3	Ficus indica	10.9
Cicca distichia	18.1	Mimusops hexandra	10.3
Phyllanthus Emblica	18.0	Flueggia leucophloea	10.3
Acacia dealbata	17.8	Eugenia caryophyl-lifolia	10.1
Terminalia belerica	17.4	Mimosa pudica	10.0
Bassia longifolia	17.7		

Particulars are given as to the % of tannin in certain Caledonian woods by U. J. Thuaw (*Collegium*, 1908, **327**, 376) and may be referred to where these woods are in question.

Catechu or **Cutch** is the dried extract from the wood of the *Acacia catechu* and allied species. It is very similar in nature to gambier. Cutch, however, generally occurs in more or less brittle, splintery masses. Gambier occurs in light, porous brown cubes, more or less adherent, or in blocks measuring 2 ft. × 1 ft. × 9 in., soft internally and wrapped in matting. *Terra japonica* is a trade-name, now somewhat obsolete, for both cutch and gambier.

In addition to a large proportion of a variety of tannin (catechu-tannic acid), catechu contains 30 or 40% of catechin (page 28), which is deposited on cooling a boiling aqueous solution.

Catechu is not infrequently adulterated; starch, sand, clay, and blood being among the materials said to be employed for the purpose. Jessart states he has met with an admixture of 60 to 70% of iron carbonate. Catechu should not yield more than 5% of *ash*, nor contain more than 12% of matter insoluble in boiling alcohol. *Starch* may be detected by treating the sample with alcohol, boiling the

insoluble residue with water, and testing the cold solution with iodine, which gives the well-known blue colour in presence of starchy matters. The presence of *ordinary tannin-matters* is indicated by the modified colour which the sample gives with ferric salts, pure catechu giving a decided green. *Blood* may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and strong smelling vapours will be produced. Aqueous solution of catechu should give with albumin or gelatin an abundant precipitate; with salts of tin and lead, yellow precipitates of various tints; and a brown precipitate with potassium dichromate. It should take a decided brown hue with alkalies, and give a greenish colour with ferric chloride. Good catechu yields at least half of its weight to ether and should be entirely soluble in boiling water, the latter solution depositing catechin on cooling. Catechu does not wholly dissolve in cold water unless it has been previously modified by age or exposure to dampness.

An aqueous solution of *Pegu* cutch gives a dense precipitate with bromine-water or cupric sulphate, neither of which reagents affects gallic, gallotannic, or pyrogallic acid. In dilute solution, Pegu cutch does not form a precipitate with potassium dichromate, but gallotannic acid does.

The proportion of tannic acid in catechu may perhaps be estimated by Löwenthal's permanganate method (page 60). The proportion of catechin is said to be roughly deduced from the volume of permanganate decolourised after removal of the minotannic acid by means of gelatin. More accurate results are obtainable by employing a moderate excess of gelatin, removing the catechin from the filtrate by agitation with ether, evaporating the ethereal liquid, dissolving the residue in warm water and titrating with permanganate.

In order to distinguish between catechu and gambier, Dieterich (*Pharm. Central.*, 1896, **2**, 855) recommends the following test: 3 grm. gambier are dissolved in 25 c.c. normal potassium hydroxide and 100 c.c. water. 50 c.c. benzene (sp. gr. 0.700) are then added, and the whole is agitated in a separating funnel. After standing the layers separate, and it is seen that the benzene shows a more or less intense green fluorescence. Acacia catechu does not show this reaction.

Kino generally occurs in irregular black fragments, but it is also met with in round cakes. Thin slices are often transparent and of a reddish colour; the powder is also red. Kino should be completely soluble in

hot water, forming a red liquid which, however, gradually becomes turbid. Kino is sometimes adulterated, the usual additions being dragon's blood, pitch, catechu, and ratanhia extract. The last substance may be distinguished from kino by touching a fragment of the sample with the tongue; kino remains reddish-brown, but ratanhia extract takes a fine bronze tint, so long as the surface is wet. The ash of kino should not exceed 3 or 4%.

Divi-divi is composed of the bean-like pods of *Cæsalpina coriaria*, a small tree found in the neighbourhood of Maracaibo and other parts of South America. The pods are about 3 in. long, brown or blackish in color, and generally folded up, or bent into the shape of a letter S. The best pods are thick and fleshy, and of a comparatively pale colour. Deep brown pods with black patches have been gathered when wet, or subsequently exposed to dampness, which injures them considerably.

Galls is a generic name applied to excrescences on plants produced by the punctures of insects for the purpose of depositing their eggs. Galls are the most valuable and important of all tannin matters.[1] *Nut-galls*, *oak-galls*, *Aleppo or Turkey-galls* are the product of the female of an insect called *cynips* (gall-wasp), which pierces the buds on the young branches of the *Quercus infectoria* and other species of oak. The eggs therein deposited soon hatch, while the bud loses its natural growth and swells out to the size of a hazel-nut. When perfect, the insect punctures a hole and escapes. Good gall-nuts should not be so pierced; they should be heavy, and of a fresh green or blue shade ("green galls"). If the insect has escaped, they are yellow and inferior ("white galls"). The best oak-galls contain 50 to 60% of gallotannic acid, and about 3% of gallic acid.

Worm-eaten galls are sometimes doctored by filling the holes with wax. The fraud may be detected by immersing the galls in boiling water, which melts the wax and renders the holes visible. Exhausted galls have been coloured by washing them with a solution of ferrous sulphate, which is readily detected by its chemical reactions.

Knoppern are galls formed from immature acorns of several species of oak, and are used for *tanning* throughout Austria. In a large number of samples of Austrian galls of the year 1884, Eitner found

[1] A sample of gall-nuts analysed by Guibourt contained: tannic acid, 65.0; gallic acid, 2.0; ellagic and luteo-gallic acid, 2.0; chlorophyll and volatile oil, 0.7; brown extractive matter, 2.5; gum, 2.5; starch, 2.0; woody fibre, 10.5; sugar, albumin, and ash, 1.3; water, 11.5%.

from 28 to 35% of tannin, the moisture being about 12% (*J. Chem. Soc.*, 1885, **48**, 947).

Chinese and *Japanese gall-nuts* are a production of the *Rhus semialata*. They are very light and hollow, and distorted by numerous protuberances, and are completely covered by a thick velvety grey down. Chinese galls are much used for the preparation of tannin, of which they contain about 70%. English galls from the common oak are much inferior to the foreign varieties. They are smooth, brown, and slightly speckled with pale brown excrescences. The Japanese are smaller, paler, and generally more esteemed.

Myrabolans are the fruit of several species of *Terminalia*. In size and shape the myrabolan resembles a slightly shriveled plum. As imported, myrabolans contain from 3 to 7% of moisture, and leave about 10% of ash on ignition. The tannin is chiefly contained in the dried pulp enclosing the stone.

Good myrabolans should be of a pale buff colour, plump, or but slightly shriveled, and free from worm-holes or blackish stains or blotches. They should be hard and firm, and when broken with a hammer should form a light-coloured dry powder and irregular fragments. If they crumble between the fingers to a dark coloured dust, or flatten under the hammer, they are inferior. The stones contain very little tannin, and hence their proportion should be ascertained by breaking 50 nuts with a hammer, clearing the stones from any adherent pulp, and weighing them separately. They may constitute from 23 to 52% of the whole fruit.

Ground myrabolans should be light in colour, dry, and free from a saline, or an intensely bitter taste. When slightly moistened and rubbed in the hand they should adhere tenaciously to the skin.

Myrabolans are sometimes mixed with earth, sand, *nux vomica*, betel-nuts, and a variety of seeds and berries. They may also be adulterated with finely ground divi-divi, wild galls, and old and worthless sumac. On scattering the powdered substance on a sheet of paper, and examining it with a lens, it will be recognised by portions of its brown, flat, smooth pea-like seeds, which from their hardness and smoothness escape being crushed to powder. The leaf stalks of sumac are readily distinguished from the torn, irregular fibre of the myrabolans.

Myrabolans possibly contain the same tannin principles as Algarobilla, and in similar quantity.

Sumac or **Sumach,** consists of the leaves, leaf-stalks, and small twigs of several species of *Rhus*. It is sometimes sold whole, sometimes coarsely bruised, but more commonly in fine powder. The best Silician sumac gives a bright green powder which has a pleasant tea-like odour. The second quality is reddish-yellow; and Spanish sumac has usually a fawn colour.

Sumac should be quite dry, and free from cakes or lumps, the presence of which shows the sample has been exposed to dampness and will probably have become seriously deteriorated. The colour should be bright. If dull, the sample is probably damaged by long keeping, or is mixed with sumac of inferior quality.

Sumac sometimes contains a notable proportion of earth or sand; 10% of ash is sometimes left on ignition.

Cape sumac (*Osyris Compressa*) contains a glucoside osyritrin. Transvaal schum sumach (*Osyris abyssinica*) is said to produce an inferior leather and colour. This tannin forms a phlobaphene more readily than the Cape variety. It also contains osyrtrin.

The analysis of Virginia sumac has been considered in some detail by Palassay (*J. Amer. Leather Chem. Assoc.*, 1910, **5**, 404).

Valonia consists of the acorn-cups of certain species of oak, chiefly exported from Smyrna, but also obtained from other parts of Asia Minor, as well as from Greece and the Grecian Archipelago. They should be of a bright drab colour. If dark they have suffered from dampness, and will be inferior in quality.

Cayota is a reddish-brown bark which comes from the southern part of Mexico, where it is used for tanning thick sole leather. It is easily powdered, has a resinous odour, and contains from 22–30% tannin.

Algarobilla consists chiefly of the pods of the *Cæsalpinia brevifolia* of Chili; it is used considerably in its native country for tanning and black dyeing. Its tannin is not a uniform body, but is a mixture one of which is a glucoside of gallotannic acid, furnishing gallic acid and sugar by hydrolysis. A second tannin, present in much larger quantity, is free from sugar. It easily separates into ellagic acid, and is identical with the tannic acid prepared from myrabolans and divi-divi.

Algarobilla gives the following reactions:

$$\left.\begin{array}{l}\text{Sulphuric acid}\\ \text{Hydrochloric acid}\\ \text{Oxalic acid}\end{array}\right\}\text{—render the solution turbid.}$$

Alkali hydroxides—liquid turns brown, slight precipitate.
Lime water—darker colour with an abundant dirty white precipitate.
Alum } —yellow-brown precipitate.
Stannous chloride }
Aluminium acetate—copious clear yellow precipitate.
Lead acetate—greenish-yellow precipitate.
Copper acetate—reddish-brown precipitate.
Iron salts—blackens solution; bluish-black precipitate.
Iron salts (in small quantity)—greenish-black colour.
Potassium dichromate—yellowish-brown liquid.
Gelatin—copious yellow-brown precipitate.

Chestnut (*Castanea Vesca*) abounds in many districts. An extract is made from the wood which is chiefly used for sole leather. It is really soluble at 60°. Sulphites and soda have been added, but they are not desirable additions. The best extracts are rich in tannins, and yet remain clear. Non-tans are said to be important in the tannin operations, but this matter is in doubt.

Particulars of the manufacture of chestnut extract in America, where the present output equals 500,000 barrels per annum, is given by Kerr (*J. Amer. Leather Chem. Assoc.*, 1910, **5**, 485). The analysis of chestnut wood is said (Alsop, *J. Amer. Leather Chem. Assoc.*, 1909, **4**, 95) to give difficulty owing to substances which yield almost infinitely to the extraction.

Canaigre consists of the ground roots of the *rumex hymenosepalum*, growing in the sandy soils of Mexico and the southwestern states of America. The wood contains 20–30% of tannin, and its extract contains 40–60% of tanin (Trimble).

Quebracho is a tree which is native of Argentina, Cuba, and other sub-tropical countries. Its name signifies "break hatchet," and refers to the great hardness of the wood. The tree grows to a considerable size, and its bark is thick and red and possesses important tanning properties. The wood has a density of 1.26, and when freshly cut has a bright orange colour which rapidly darkens to a reddish shade on exposure. The tannin from the bark and wood is readily extracted by boiling water. The ground wood contains about 18% of tannin, which, however, is reduced on exposure to the air for any length of time. The extract, 30° Be., contains about 50–56% of tannin, while the dried extract will contain over 60% of tannin.

An infusion of quebracho gives the following reactions:

Dilute sulphuric acid and hydrochloric acid, a bright orange precipitate.

Alum to an alkaline solution, an orange-red lake.

Aluminium acetate, a yellow precipitate.

Stannous chloride, an orange-yellow precipitate.

Stannic chloride, a darker precipitate.

An iron salt, in small quantity, a blue-black precipitate.

An iron salt, in large quantity, a grey precipitate.

Potassium dichromate, a reddish-brown precipitate.

Copper salts, a greenish precipitate.

Lead acetate, a bright precipitate.

Aluminium sulphate, a greyish precipitate.

Palmetto is an evergreen palm-like shrub, which grows abundantly in the southern states of America. The extract contains from 8 to 12% of tannin and is employed for tanning leather.

Mimosa, Acacia, Wattle Bark.—Wattle bark is obtained in Natal and Australia, and more recently in East African protectorate, transvaal, etc. It contains 24–42% of tannin and 10–12% non-tannins. The maximum yield is obtained from 6–8 year old trees, but it yields at 4 years. It produces leather of good quality and texture and has no tendency to harshness (*Bull. Imp. Inst.*, 1910, **8**, 245).

Mimosa (*Acacia*) gives a light reddish colour to leather. The tannin is readily soluble and extracts are obtained up to 8–10% before concentrating. The liquors keep well and have high weighting power almost equal to quebracho. It is chiefly suitable for sole leather.

On an average of 260 samples Peassler gives the following figures for mimosa barks:

	Filter method.	*Shake method.*
Tannins	33.0 (22–48)	31.5 (20.5–46.5)
Non-tannins	9.5	11.0
Insoluble	43.0	43.0
Water	14.5	14.5

Mimosa extracts give the following average figures: Tannins, 31.5, non-tannins, 9.5; insoluble, 1.0; water, 58.0%; ash, 1.5; sp. gr., 21–28 Bé.

Mangrove. West African Mangroves, *Red* (*Common*) *and White.*—The red variety grows in the mud by the sea, the wood is very hard, the heart being dark red. The young wood is yellow. The bark is said to contain 17.5% tannin (Moller) or 39% (Paessler) and

is used locally for colouring fishing nets. This red colour is an objection in tanning.

Trimble found the following reactions in a 1% solution:

Ferric chloride,	Dirty green ppt.
Lime-water,	Pink ppt.
Bromine water,	Yellow ppt.
Uranium acetate,	Red-brown colour.

No sugar was found associated with the tannin, which is a catechol derivative. It is said to be the only tannin which gives a precipitate with sulphuric acid.

The white variety (*Laguncularia racemosa*, Gr.) contains a pyrogallol tannin. It is said to be useful in combination with divi-divi, producing a light leather.

There will probably be an extended use for this in the future. The composition of these 2 varieties has been given as follows:

	White mangrove.	*Red mangrove, West African.*
Water	10.42%	10.42%
Tannins	22.80%	9.10%
Org. non-tannins	3.06%	13.64%
Inorg.	2.95%	2.52%
Insol. at 100°	62.77%	64.32%

Qualitative Recognition of Tannin Materials.

The following tables, due to Procter, shows the behaviour of infusions of a number of commercial tannin matters with various reagents. The infusions must be very weak, not exceeding 1.002 sp. gr., or precipitates may be formed where mere colouration or clouding is described as occurring. By means of the table, the origin of any simple tannin infusion is said to be ascertained, but in the case of mixed infusions the indications are less reliable. In such cases, colour-reactions are misleading and it is safer to rely on the direct test of precipitate or no precipitate, colouration or no colouration, without regard to the tint.

In some cases, only negative indications are recorded, and the material cannot be positively identified in admixture with other tannin matters giving positive indications with the same reagents. Thus an infusion of myrabolans could not be distinguished with certainty from an infusion of divi-divi, where any other material, such as gambier,

was present, which gives a deep colouration with concentrated sulphuric acid.

In addition to the reactions described in the table, the identification of the products of the action of heat on tannins, and of their treatment with dilute acids and fusing alkali hydroxide, affords a valuable means of identification.

Most, if not all, of the ordinary varieties of tannin give with an ammoniacal solution of potassium ferricyanide a deep red colouration, rapidly becoming brownish, especially on addition of excess of the reagent.

The extract from a bark yields more ash than that from a wood.

Reagent	Myrabolans	Divi-divi	Valonia	Oak-bark	Chestnut wood (extract)
Boiled with equal volume of dilute sulphuric acid (1 to 9).	Pale deposit (ellagic acid) on cooling.	Pale deposit (ellagic acid) on cooling.	Slight pale deposit.	Slight pale deposit or turbidity on cooling.	No deposit.
Bromine water.	No precipitate.	No precipitate.	No precipitate.	Pale precipitate.	No precipitate.
Dilute ferric chloride.	Blue-black precipitate.	Dark blue precipitate.	Blue - black precipitate.	Bluish-black precipitate.	Blue-black precipitate.
On adding ammonia.	Brown precipitate.	Dark red precipitate.	Red - brown precipitate.	Red-brown precipitate.	Purple precipitate.
Solution tartar emetic.	No precipitate.	Faint clouding.	No precipitate.	No precipitate.	Slight clouding.
Add ammonium chloride.	Light precipitate.	Dense precipitate.	Pale precipitate.	Whitish precipitate.	Pale precipitate.
Copper sulphate.	Faint clouding.	Slight green precipitate.	No precipitate.	Slight precipitate.	No precipitate.
On adding ammonia.	Dense dark precipitate.	Dense dark precipitate.	Dark reddish precipitate.	Brown precipitate.	Light brown precipitate.
Lime-water......	Yellow precipitate turning greenish.	Yellow precipitate turning purple.	Yellow precipitate turning red purple.	Brown precipitate.	White precipitate turning light blue.
Ammonium molybdate in nitric acid.	Dirty yellow precipitate.	Dark greenish precipitate.	Dark greenish precipieate.	Greenish precipitate.	Yellow colour.
With sodium sulphide exposed to air.	Yellow colour.	Yellow colour.	Turns purplish-red.	Turns red.	No change.
Add concentrated sulphuric acid to 1 drop of infusion.	Yellow colour.	Intense crimson.	Deep yellow.	Deep red precipitate on dilution.	Light yellow.
Lead nitrate.	Light yellow precipitate.	Dark yellow precipitate.	Pale precipitate.	Brown precipitate.	White precipitate.
Cobalt acetate...	Buff precipitate.	Buff pink precipitate.	Dirty pink precipitate.	Brown precipitate.	Flesh-coloured precipitate.
Manganese acetate.	Yellow precipitate.	Yellow precipitate.	Dirty yellow precipitate.	Brown pretacipitate.	White precipitate.
Uranium acetate.	Dark red colour.	Dark red colour.	Dark red colour.	Dark brown precipitate.	Crimson colour turning dark red.
Ammoniacal picric acid solution.	No precipitate.	No precipitate.	Brown precipitate.	No precipitate.	No precipitate.
Potassium dichromate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.

Hungarian larch (extract)	Hemlock (extract)	Mimosa bark	Cutch (Pegu)	Gambier (cube)	Gallotannic acid, 1%
Yellow flocculent deposit separates quickly.	Abundant red flocculent deposit.	Heavy red deposit on cooling.	Light red deposit on cooling.	Reddish deposit on cooling.	Usually some pale deposit.
Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	No precipitate.
Dull brown precipitate.	Dirty green precipitate.	Full brown precipitate.	Green-black precipitate.	Intense green colour.	Blue-black precipitate.
Dull red precipitate.	Reddened precipitate.	Purple colour.	Dark red precipitate.	Reddened.	Reddened precipitate.
No precipitate..	No precipitate.	White precipitate.	No precipitate.	No precipitate.	No precipitate.
Pale precipitate.	Slight pale precipitate.	Dense white precipitate.	Pale precipitate.	Faint clouding.	White precipitate.
Slight cloud.	Pale precipitate.	Slight precipitate.	Dense precipitate.	Profuse precipitate.	No precipitate.
Deep blue colouration.	Dark green colouration.	Deep red precipitate.	Deep violet colouration.	Dark green colouration.	Brown precipitate.
Dirty brown precipitate.	Brown precipitate.	Slight reddish precipitate.	Slight cloud, soluble in excess.	No precipitate.	Pale precipitate turning blue.
Slight clouding.	Slight precipitate.	Brown precipitate.	Slight cloud, soluble in excess.	No precipitate.	Yellow colour.
No change......	No change.	Turns red.	Slight reddening.	No change.	No change.
Dark brown or crimson.	Intense crimson.	Intense purple-red.	Deep red, no precipitate on dilution.	Dark brown or crimson.	Yellow.
Pale precipitate.	Pale precipitate.	Clouding.	No precipitate.	Faint clouding.	White precipitate.
Purplish precipitate.	Purple precipitate.	Brown precipitate.	Brown precipitate.	No precipitate.	Purple precipitate.
Slight clouding.	Slight precipitate.	No precipitate.	No precipitate.	No precipitate.	White precipitate.
Slight darkening.	Light brown precipitate.	Dark red colour.	Dark red colour.	Dark red colour.	Crimson colour. Brown precipitate.
No precipitate.	Clouding.	No precipitate.	No precipitate.	No precipitate.	No precipitate.
No precipitate.	Brown precipitate slowly formed.	Brown precipitate.	Brown colour.	Brown precipitate slowly formed.	Brown precipitate.

The ash of an oak or pine extract may contain manganese and has a green colour, or becomes green on being fused with sodium carbonate and a little potassium nitrate.

On shaking a concentrated solution of quebracho extract with ethyl acetate, the ethereal layer becomes at first green and then brown.

The bark and extract of the American chestnut oak (*Quercus castanea*) contains a substance exhibiting, like æsculin, a powerful blue fluorescence, especially in alkaline solution.

Pure tannins yield different kinds of derivatives with phenylhydrazine; but as these do not crystallise no satisfactory separation can be made in this manner.

Sumac extracts are distinguished by a peculiar tarry smell, and yield a high percentage of ash.

Proctor (*J. Soc. Chem. Ind.*, 1894, **13**, 487) gives the following tables for the qualitative recognition of tanning materials:

TABLE I.

Bromine water produces a precipitate.		Bromine water produces a precipitate.		Bromine water produces no precipitate.	
Iron-alum gives greenish-blacks.		Iron-alum gives blue or purplish-blacks.		Iron-alum gives blue-blacks.	
(Catechol tannins.)		(Mixed and doubtful.)		(Pyrogallol tannins.)	
$CuSO_4$ with excess of NH_4OH.		$NaNO_2$ with 5 drops of N/10HCl.		$NaNO_2$ with 5 drops of N/10HCl.	
Precipitate redissolves.	Precipitate does not redissolve.	No reaction, or, at most, darkening.	Colour change from red towards blue or Green.	Colour change through Red to Blue.	No reaction.
1α	1β	2α	2β	3α	3β
Table II.	Table III.	Table IV.	Table V.	Table VI.	Table VII.

TABLE II.

Class 1α	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
Cutches from Ac. catechu wood.	Green-black.	Pp.	No react. darkens.	Pp. redissolves red-violet colour.	No react.	Deep violet-red.	Reddens.	Red-brown colour.	Reddish pp. slowly formed.
"Thann leaf" extract (a cutch substitute).	Olive-black pp.	Pp.	Do.	Pp. redissolves brown colour.	No react.	No react.	No react.	Crimson, dilute pink.	No pp.
"Turwar" bark (*Cassia auriculata*).	Green-black.	Pp.	Do.	Pp. redissolves red violet.	No react.	Trace.	Pink colour.	Crimson.	Reddish pp.
"Gambene" extract (a gambier substitute).	Green-black colour.	Pp.	Do.	Do.	No react.	No react.	Slight pink colour.	Crimson, dilute pink.	Do.
"Teugah" bark (*Ceriops Candolleanna*).	Do.	Pp.	No react. darkens pp.	Do.	Pink colour.	No react.	Pink colour.	Crimson.	Bright red pp.
Bark (*Acacia leucophlæa*)	Do.	Pp.	No react.	Do.	Do.	Slow violet react.	Pink colour.	Crimson, dilute pink.	Dull brown pp.
Bark (*Soymida febrifuga*)	Do.	Pp.	No react.	Pp. redissolves red-brown.	Do.	No react.	Pink colour.	Crimson.	Red brown.
Cork bark (*Quercus suber*).	Green-black colouration.	Pp	Reacts somewhat.	Pp. redissolves brown.	No react.	No react.	Reddens.	Crimson, dilutes pink.	Reddish brown pp.
Green oak (Ital.) (*Quercus Ilex*.).	Do.	Pp.	Reacts faintly, if at all.	Do.	No react.	No react.	Reddens.	Do.	Do.
Garouille (root bark of Kermes oak) (*Quercus Coccifera*).	Do.	Pp.	Reacts?	Do.	No react.	No react.	Reddens.	Do.	Do.

TABLE II.—*Continued.*

Class 1 α	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
[1]Quercitron bark (*Quercus Tinctoria*).	Green-black colouration.	Pp.	Reacts somewhat.	Pp. redissolves brown.	Light green.	No react.	Doubtful.	Crimson, dilutes pink.	Reddish brown pp.
Gambier (ext. of leaves of *Nauclea gambir*).	Deep green colouration.	Pp.	No react. darkens.	Pp. redissolves olive-green.	Yellow.	Deep violet-red.	Yellow.	Crimson, dilutes brown.	No pp.
[2]"Pruim bast" (leaves of *Colpoon* or *Osyris compressa*).	Green-black.	Pp.	No react.	Pp. redissolves green.	No react.	Pink.	Yellow.	Do.	Light yellow pp.
[3]"Koko." Natal (leaves of *Celastrus buxifolia*).	Do.	Pp.	No react.	Do.	No react.	No react.	Yellow.	Dark brown.	Bright yellow pp.
Larch bark (*Larix Europæa*).	Green-black colouration.	Pp.	No react. darkens.	Pp. redissolves olive-green.	Pink colouration.	No react.	No react. darkens.	Deep red-brown.	Rusty pp.
Hemlock bark (*Tsuga* or *Abies Canadensis*).	Olive-green reddish pp.	Pp.	No react., pink with $NaNO_2$.	Pp. redissolves neutral tint.	Do.	No react.	Reddens.	Crimson, dilutes pinkish.	Red-brown pp.
"Larch" extract from *Abies excelsa*.[4]	Green-black or brown.	Pp.	No react.	Pp. redissolves olive-green.	Do.	No react.	Darkens.	Deep red-brown.	Brown pp.

[1]Dyes yellow with Al and Sn mordants.
[2]Used at Cape of Good Hope as sumac.
[3]Used in Natal as sumac substitute.
[4]*Fichte*, *Rothtanne*, Norway or common spruce. *Abies pectinata* the *Weiss* or *Edel-Tanne* or silver fir, is said to give a blue-black colour with iron.

TABLE III.

Class I β	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
Willow bark (Russian. Sp. unknown).	Green-black.	Pp.	No react.	Dense pp.	No react.	Violet faint.	Pink colouration.	Red-brown not intense.	Slight greyish pp.
Acacia Angica or *Piptadenia macrocarpa*.	Do.	Pp.	No react.	Dense chocolate pp.	Pink or violet colour.	Do.	Reddens somewhat.	Crimson dilutes pink.	Reddish pp.
Acacia catechu bark.	Do.	Pp.	No react.	Dense violet-black pp.	Possible trace.	Trace.	Pink colour.	Red-brown.	Flesh colour pp.
"Thorn tree" bark (*Acacia horrida*) (Cape).	Do.	Pp.	No react. darkens.	Dense pp.	No react.	Doubtful.	Pink colour.	Dull crimson not intense.	No pp.
Mangrove bark extract (*Rhizophora mangle*).	Do.	Pp.	No react.	Reddish-black.	Slight reddening.	No react.	Slight reddening.	Red-brown.	Red pp. darkened by excess.
Quebracho wood extract (*Quebracho or Loxopterygium Lorentzii*).	Green-black colouration.	Pp.	No react.	Dense pp.	Pink colour pp.	Trace.	Doubtful.	Crimson colouration dilutes pink.	Light brown pp.
"Sugar bush" bark (Cape) (*Protea mellifera*).	Green-black.	Pp.	No react. darkens.	Dense pp.	No react.	Trace.	Doubtful.	Red.	Yellow-brown pp.
"Waagenboom" (Cape) (*Protea grandiflora*).	Do.	Pp.	Do.	Dense pp.	No react.	Trace.	Pink colour.	Crimson dilutes pink.	Light yellow pp.
"Kruppelboom" (Cape) (*Leucospermum conocarpum*).	Do.	Pp.	Do.	Dense pp.	No react.	Violet distinct.	Pink colour.	Do.	Slight greyish pp.
"Silver tree" (Cape) (*Leucodendron argentea*).	Do.	Pp.	Do.	Dense pp.	No react.	No react.	Pink colouration.	Do.	Flesh colour pp.
[1]Chestnut oak (*Quercus Castanea*).	Olive-green colouration.	Pp.	Reacts distinctly.	Decided pp. Insoluble in excess.	No react.	No react.	Reddens.	Crimson dilutes pinkish.	Reddish-brown pp.

[1] Infusions fluoresce, especially with ammonia.

TABLE IV.

Class 2a	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
"Skens," cypress sumac (possibly *Coriaria myrtifolia*).	Blue-black pp.	Pp.	No react.	Dark pp.	No react.	No react.	Yellow.	Yellow-brown.	Yellow pp. darkening.
Kliphaut bark[1] (*Rhus Thunbergii*).	Blue-black.	Pp.	No react.	Dense dark pp.	No react.	No react.	Pink.	Dull crimson dilutes orange.	Pinkish pp.
Canaigre (root of *Rumex hymenosepalus*).	Blue-black pp.	Pp.	No react.	Dense dark pp.	No react. clouds.	Trace violet.	Slight darkening.	Yellow-brown.	Pink colouration greyish pp.
"Talwaan" or "Elandsbontjes" (root *Elephantorrhiza Burchellii*).	Blue-black pp.	Pp.	No react. Darkens.	Dense dark pp.	No react.	Trace violet.	Pink.	Red.	Reddish-brown pp.
Mimosa or Wattle barks (Various Austral. *Acaciæ*).	Dirty violet pp.	Pp.	No react.	Dense purple brown pp.	Slight reddening.	Sometimes trace.	Reddens.	Crimson dilutes pink.	Reddish or yellow-brown pp.
Babool bark. India (*Acacia Arabica*).	Do.	Pp.	No react.	Dense dark pp.	Some trace	Faint trace	Slight darkening.	Crimson dilutes orange.	Dark reddish-brown pp.
Dark red Austr. bark (probably an *acacia*).	Do.	Pp. needle crystals.	No react.	Deep violet pp.	No react.	Faint trace	Orange-pink.	Crimson dilutes pink.	Bright violet pp.
"White bark" *Algaroba blanca*. South America (A *prosopis* or *acacia*).	Do.	Pp.	No react.	Reddish-black pp.	No react.	Violet.	Reddens strongly.	Do.	Red pp. turning. violet.

[1] Used at Cape of Good Hope.

TABLE V.

Class 2β	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
English oak (*Quercus Robur*).	Blue-black (green with excess).	Pp.	Reacts somewhat.	Slight pp. Dark brown pp.	No react.	Faint react.	Reddens.	Crimson dilutes pink.	Reddish-brown pp.
Jaft or Dchit.[1] Supposed oak product.[2]	Blue-black pp.	Pp.	Reacts red-blue.	Brown pp. Dark brown pp.	No react. Dark brown pp.	Do.	Some darkening.	Do.	Do.

[1] A Persian product, dark scales very rich in tannin about (40%).
[2] Strong infusions, dry whitish and iridescent.

TABLE VI.

Class 3α	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
Aleppo galls (of *Quercus infectoria*).	Blue-black pp.	No pp. slight scum.	Reacts red to blue.	Dark pp. insoluble.	Light yellow pp.	No react.	No react.	Greenish to dirty yellow.	Pale pp. turning bluish-green.
[1]Sumac (leaf of *Rhus coriaria*).	Do.	No pp.	Reacts feebly.	Dark-brown insoluble pp.	No react.	No react.	No react.	Yellow.	Yellow pp. turning bright green.
[1] Myrabolans (*Terminalia chebula*).	Do.	No. pp.	Reacts red to blue	Dark insoluble pp.	No react.	No react.	Yellow.	Yellow.	Yellow pp. turning. greenish.

[1] Dyes yellow on Sn. mordants.

TABLE VI.—*Continued.*

Class 3α	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
Pomegranate rind (*Punica granatum*.)	Blue-black pp.	No pp.	Reacts red to blue.	Dark-brown insol. pp.	No react.	No react.	No react.	Orange-brown.	Bright yellow pp. turning red with excess.
Algarobilla (*Cæsalpinia brevifolia*).	Do.	No pp.	Do.	Dense dark pp.	No react.	No react.	Deep yellow.	Deep yellow-brown.	Bright yellow pp. darkens some.
[1]Divi-divi (*Cæsalpinia coriaria*).	Do.	No. pp.	Do.	Do.	No react.	No react.	No react.	Crimson.	Yellow pp. turning red-purple.
Algarobo (*Prosopis dulcis*).	Do.	Do.	Red to olive.	Do.	No react.	No react.	Yellow.	Yellow to olive.	Yellow pp. turning black.
Valonia (*Quercus Aegilops*).	Do.	Do.	Red to blue.	Dark, reddish pp.	No react.	No react.	Purplish-pink.	Deep yellow.	Yellow pp. turning red-purple.
[2]"Oakwood" extract (oak or chestnut).	Do.	Do.	Do.	Purple-brown pp.	No react.	No react.	Reddens.	Yellow-brown.	Do.

[1] Moderately strong potassium nitrate solution precipitates divi, but not *dilute* oak-wood solutions; pp. soluble in hot or *much* cold water.

[2] *Crude* chestnut wood extract may be distinguished from oakwood by its violet coloured indication with ammonium sulphide.

TABLE VII.

Class 3β	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
Pure gallotannic acid....	Blue-black pp.	No pp.	No react.	Dark pp.	No react.	No react.	No react.	Yellow.	Pale pp. turning blue.
Babool pods (*Acacia Arabica*).	Blue-black.	No pp.	No react. darkens.	Dark green colour.	No react.	Faint violet.	No react.	Reddish violet.	Pink colour. No pp.

TABLE VIII.

Class 3β	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime-water
Catechol..............	Dark green colour.	No pp.	Turns yellow.	Green colour.	No react.	No react.	No react.	Green colour.	No react.
Protocatechuic acid.....	Dark green colour.	No pp.	Turns brown.	No pp.	No react.	No react.	No react.	No react.	No react.
Phloroglucinol..........	No react.	Bulky white pp.	Turns olive-green.	No pp.	No react.	Red violet colour.	No react.	Slight yellow.	No react.
Pyrogallol..............	Blue-black turning green and brown.	No pp.	Turns yellow.	Brown colour.	No react.	No react.	No react.	Brown colour.	Violet rapidly turning brown.
Gallic acid.............	Blue-black colour.	No pp.	Turns brown.	Brown colour.	No react.	No react.	No react.	No react.	White pp. rapidly turning blue.

TABLE IX.

REACTIONS OF PURIFIED OAK BARK TANNINS (TRIMBLE, *Tannins*, VOL. 2., P. 88).

	Ferric alum	Bromine water	Nitrous acid	$CuSO_4$ + NH_4OH	$SnCl_2 + HCl$	Deal shavings and HCl	Na_2SO_3	Lime-water
Black oak (*Q. tinctoria*)	Green colour and pp.	Yellow pp.	Brownish-yellow pp.	Pp. Green colour.	Yellow with some pink.	Violet colour.	Yellow colour.	Pp. turning pink then red.
Pin oak (*Q. palustris*)	Green colour and pp.	Yellow pp.	Pinkish colour changing to brown pp.	Pp. Brownish-green colour.	Pink colour.	Violet colour.	Pink colour.	Pp. turning pink then red.
Scarlet oak (*Q. coccinea*)	Bluish-green colour Green pp.	Yellow pp.	Brown pp.	Pp. Green colour.	Pinkish colour.	Violet colour.	Pinkish yellow colour.	Pp. turning reddish.
Spanish oak (*Q. falcata*)	Green colour and pp.	Yellow pp.	Brown pp.	Pp. Red-brown colour.	Yellow colour some pink.	Violet colour.	Yellow with pink streaks.	Pp. turning reddish.
White oak (*Q. alba*)	Green colour and pp.	Yellow pp.	Brown pp.	Pp. Brown-green colour.	Pinkish colour.	Violet colour.	Pinkish colour.	Pp. turning pink.
Willow oak (*Q. phellos*)	Green colour and pp.	Yellow pp.	Brown pp.	Pp. Red-brown colour.	Very yellow colour.	Violet colour.	Yellow with pink streaks.	Pp. turning green, liquid reddish.
Chestnut oak (*Q. prinus*)	....	Yellow pp.	....	No pp. Greenish-brown colour.	....	....	....	Pp. turning pink.
Swamp white oak (*Q. bicolor*).	....	Yellow pp.	....	....	....	....	....	Pp. turning pink.
English oak (*Q. robur*)	Bluish-green colour. Green pp.	Yellow pp.	Pink colour changing to brown pp.	Pp. Red-brown colour.	Decided pink colour.	Violet colour.	Pink colour.	Pp. turning pink.
Indian oak (*Q. semicarpifolia*).	Green colour and pp.	Yellow pp.	Brownish-yellow pp.	....	Pink colour.	Violet colour	Yellow colour.	Pp. turning pink.

The reagents employed in the above tests are prepared and used as follows:

Ferric alum, a 1% solution. This salt appears to be better than ferric chloride or acetate. It may be reasonably assumed that any tannin which gives a distinctly greenish-black with iron is a catechol derivative, but there are a large number of materials, especially among the acacias or mimosas, which give purplish blacks, but are almost certainly catechol tannins; and, on the other hand, the oak barks which Trimble has proved to be catechol tannins, and most of which give green-blacks with iron, also yield bloom, or ellagic acid, and are therefore also allied to gallic acid. Another reagent is therefore employed in the preliminary classification, viz.,

Bromine Water.—It is best to add this drop by drop to 2 or 3c.c. of the infusion in a test-tube until the solution smells strongly. In some cases the precipitate is slight, or forms slowly, and occasionally it is crystalline and on this account less easily recognised, but it is usually a distinct yellow or brown flocculent one. In general terms it may be said to be a reagent for the catechol tannins; precipitating all which give green-blacks with iron, and many which give blue or violet-blacks, which are reasonably suspected of containing catechol. It does not precipitate any recognised pyrogallol tannin, but several which yield ellagic acid (bloom), such as oak barks.

Nitrous Acid Reaction.—This reaction is obtained by adding to a few c.c. of the very dilute infusion in a porcelain basin a distinct excess of freshly prepared solution or a few crystals of sodium or potassium nitrite, and then 3–5 drops of N/10 sulphuric or hydrochloric acid. In typical cases the solution instantly turns pink or crimson, and slowly changes through purple to a deep indigo-blue; but in others, as sumac, where the reaction is feeble, and masked by other changes, the final colour is green or even brownish. In a large number of cases, nitrous acid produces a yellow or brown colouration or precipitate, but "reaction" in the tables invariably means a series of colour-changes as above described. The reaction is given by all tanning materials which yield ellagic acid or "bloom," but not by ellagic acid itself, nor by pure gallotannic acid. It is therefore probably a reaction of ellagitannic acid, and is valuable for subdividing the mixed and pyrogallol tannins. It may also be obtained faintly from some of the oaks in Class 1β.

Copper Sulphate and Ammonia.—A 1% solution of copper sul-

phate is employed, and is added to the tannin solution first, followed by ammonia in slight excess.

Stannous Chloride and Hydrochloric Acid.—This reagent consists of a strong solution of stannous chloride in concentrated hydrochloric acid. If about 10 c.c. of this are added to 1 c.c. of the tanning material infusion, in a procelain basin, and allowed to stand for 10 minutes, coniferous tans, mimosas, and some others give a very marked pink colouration. This is specially distinct in the case of larch bark. If a small piece of larch-tanned leather be steeped in the reagent, the colouration appears very strongly.

Deal Shaving and Hydrochloric Acid.—A shaving or slip of any pine wood is moistened with the infusion, and then, either before or after drying, is again moistened with concentrated hydrochloric acid. In the case of cutch and gambier, and a few other materials, and of solution of phloroglucinol itself, the spot becomes at once a bright red or violet, but in many cases the indication is faint, and only appears after some hours. It probably always indicates the presence of phloro-glucinol. The statement that catechol gives a similar reaction appears to be incorrect.

Sodium Sulphite.—A few drops of the tannin solution are placed in contact with a crystal of sulphite on a tile. Many tanning materials produce red or pink colourations, but in no case so marked an indication as valonia.

Sulphuric Acid.—About 1 c.c. of concentrated acid is cautiously added to a few drops of the tannin solution in a test-tube so that the acid forms a layer beneath the tannin. The ring of colour at the junction of the 2 liquids is noted, and then they are mixed by shaking and diluted with water.

Lime-water is a most useful reagent. The action is best seen in a shallow porcelain dish, and time must be allowed for the change to take place.

The infusions of tanning materials employed should contain about 0.6 grm. of dry soluble matter in 100 c.c.

Most tannins possess dyeing properties, giving a variety of brownish or yellowish shades on textiles. There seems to be an intimate connection between the colouring principle and the tannin matters contained in the same plants. On decomposition, the same acid, and in some cases the same phenol, is obtained from both. The following

table will show the correspondence in the decomposition products of the tannin and its respective colouring matter:

	Tannin	Decomposition product of tannin	Colouring matter	Decomposition product of colouring matter
Quebracho Colorado.	Quebracho-tannic acid.	Phloroglucinol and protocatechuic acid.	Fisetin........	Resorcinol and protocatechuic acid.
Rhus Coriaria.. Rhus Cotinus.	Gallotannic acid.	Gallic acid ..	Myricetin....	Phloroglucinol and gallic acid.
Gambier Catechu. Acacia catechu.	Catechin	Phloroglucinol and protocatechuic acid.	Quercetin...	Phloroglucinol and protocatechuic acid.
Divi-divi.......	Ellagitannic acid.	....	Ellagic acid..	

A. G. Perkin (*Trans.*, 1897, **71**, 170) finds that the colouring principle of Cape sumac is a glucoside, osyritrin, $C_{27}H_{30}O_{17}+2H_2O$, which is decomposed by acid into quercetin and dextrose. Venetian sumac showed the presence of myricetin and not quercetin as stated by Löwe.

Valonia, divi-divi, myrabolans, algarobilla, and gall-nuts, owe any dyeing powers to ellagic acid, and contain no member of the quercetin group.

Andreasch (*Gerber*, 1894, **20**, 195 and 207) gives in tabular form the reactions in alcoholic solutions. These have been used by the Vienna Institute for the examination of such extracts obtained from finished leathers.

Analytical Methods for Estimating Tannic Acids and Tannins.

A number of methods have been described for estimating tannin and assaying tannin-yielding materials. In many instances the fact has been overlooked that gallic acid, while behaving in many respects like tannin, does not form stable insoluble compounds with gelatin and albumin, and hence is considered valueless for the purpose of tanning.[1]

1 It must, however, be remembered that gallic acid is carried down or absorbed, by a tannin-gelatin coagulum and may then play some definite, if obscure, part in the process of tanning when present in the non-tans.

These and the following points must be carefully considered when deciding on the selection of any process of analysis for special purposes. It must be remembered that the chemistry of tanning is so involved that only practical trial and experience can confirm the relative values of different tannin materials. For the purpose of the tanner a purely empirical method of analysis is still adopted. The "active" tannic acids are absorbed under certain artificial, but definitely laid down conditions. This has been found to be absolutely necessary in order that different analysts may obtain similar results when reporting on the value of these materials. Under these specific conditions it is assumed that the value of any extract or tanning material may be ascertained and results obtained which will indicate its relative value in terms of this absorption. The necessary details are confirmed and varied by International Conferences, both in Europe and America.

For the dyer these "official" figures may have little value in cases in which dyeing black on iron mordants, or the weighting of the silk fibre is the object aimed at, or when mordanting cotton for dyeing light shades with basic dyes. Under these conditions a process which is in some way comparable to the conditions in practice may be more suitable, as in the corresponding case of the leather industry. The hide-powder results may therefore be of minor value to the "lake manufacture," or the black silk dyer; and for special purposes one of the other processes of analysis may be selected and supplemented by some practical test, such as the actual weighting of a silk yarn under standard conditions, or the dyeing of the same on one or more mordants, or the treating of cotton yarn in some similar way to that adopted in working on the large scale.

Owing to the highly organised condition and official status of the hide-powder process these points are sometimes overlooked.

Sampling of tannin materials is often a troublesome operation, and together with the difficulty attending complete extraction is a fertile source of error. The official associations have stringent conditions which cover this operation and these must be referred to.

When available, a steel mill is the best means of roughly pulverising most tannin materials. With the exception of barks, the grinding can be effected by a disintegrator with fine screens, taking great care to prevent the escape of dust. Barks may be sampled by cutting each fragment with a small circular saw or rasp driven by a lathe, and collecting the dust.

In sampling valonia care must be taken to get a due proportion of the beard, and in taking myrabolans it must be remembered that the bad berries are light and apt to work toward the top of the bag. The sample being partially reduced by one of the above means, the moisture (usually 15 to 16%) must be estimated by drying at 100°.

Sampling Extracts in Barrels.—Lepetit (*Collegium*, 1910, 382) proposes that in the place of the official regulations the total number of casks to be sampled shall be the square root of the total number less one, instead of 5%. The barrels are rolled a distance of 20 metres and left to stand for a few minutes first on one end and then on the other. The bung is removed and 2 buckets full of extract removed, the contents of the cask being shaken before removing the sample to be tested. This method is said to occupy much less time and to be more efficient than the official European method.

The extraction of tannin-matters is better effected by treating the sample at once with a large quantity of water than by repeated treatment with smaller quantities. Reference may be made to the official methods of extraction for analysis.

The analysis of chestnut wood is said (Alsop, *J. Am. Leather Chem. Assoc.*, 1909, **4**, 95) to give difficulty owing to substances which yield almost indefinitely to the extraction.

Tannin solutions free from colouring matters have been prepared by adding zinc sulphate and ammonium sulphate to the solution; tannate of zinc is thus precipitated, which is washed with a very dilute solution of ammonia. It is then suspended in 5 times its volume of water and decomposed by dilute sulphuric acid. Barium sulphide is added till no further precipitate is formed. The precipitate, which consists of zinc sulphide and barium sulphate, is removed, and an almost colourless solution of tannin remains. This method has been applied to the manufacture of *colourless extracts.*

Tan liquors have been decolourised by treating with lead nitrate, and afterward adding alum and borax. Strontium hydrate and carbonate have also been used for the precipitation of the colouring matters; sulphuric acid being added to the filtrate to remove the excess of strontium salt. Clarification is also accomplished by electrolysing the liquid to which has been added oxalic acid and sodium chloride. Sumac may be decolourised with fair results by the use of ox-blood.

Grasser recommends a special apparatus for tannin extraction (*Collegium*, 1910, 345) in place of Procter's sand-filter apparatus.

It consists (see Fig. 1) of 2 copper cylinders, the inner one being supported by the projections *e*. The lower extremity of the inner tube is packed with cotton wool at *o*. The material to be extracted is contained in this inner tube. Water, at a gradually increasing temperature (from 25°–60°) is poured on the substance until 400 c.c. has passed, when the litre flask at the bottom is replaced by an Erlenmeyer flask containing 250 c.c. of water. A condenser is attached and extraction takes place for one hour and the extract is added to the first 400 c.c. Re-extraction takes place with a fresh 250 c.c. of water until the material is exhausted. With spent material it is sufficient to boil up with 300 c.c. of water.

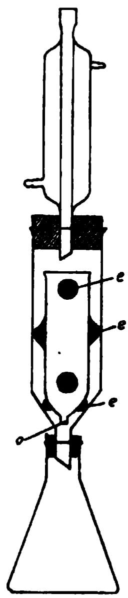


FIG. 1.

Of the numerous methods which have been devised for the assay of tannin-matters, many have been based on the principle of precipitation of the tannin by a solution of gelatin or its absorption by a gelatinous substance. In some cases the weight of the precipitate formed, or the increase in the weight of the solid gelatinous substances has been found, but the better plan is to ascertain the quantity of tannin precipitated by comparing the solution after the treatment with the original untreated solution. This is done by Hammer by taking the sp. gr.; by Simand and Weiss by weighing the solid matter left on evaporation; and by Löwenthal by determining the volume of standard permanganate solution decolourised by the solution before and after removal of the tannin. These methods, which appear simple enough in principle, are in practice surrounded with very considerable difficulties, especially when gallic acid or other impurities are present. For instance, the disturbing action of gallic acid on the ordinary hide-powder process may be indicated by the following figures, the estimation of pure gallic acid being attempted in different ways with the following results:

Dreaper method (lead separation) shows......	0.0% tannic acid.
Dreaper method (hide powder separation)	45.6% tannic acid.
Hide-powder process........................	27.0% tannic acid.

These variations were found on further investigation to be due to two distinct causes: 1. Absorption of gallic acid by hide powder; 2. solubility of hide powder in gallic acid solution. In the first case

neither of these defects are present, in the second the absorption of the gallic acid is estimated, in the third this result is modified (to the extent of 18.6%) by the solubility of the hide powder which partially "corrects" the error in the second case, as the non-tannins are estimated by direct weighing (Dreaper, *Chem. News*, 1904, **90**, 3).

These results are given, as they indicate the nature of the controlled action of the recently introduced chrome or "treated" hide powders. The chroming action, by rendering the hide powder less soluble, tends to correct the above error (18.6%), and at the same time by reducing the hydration of the hide material, correspondingly reduces the ratio of the absorption of gallic acid without materially decreasing that of the tannic acid. The res lt of variations in the hydrogel state of such precipitating media (as gelatin or albumin) has been investigated by Dreaper and Wilson (*J. Soc. Chem. Ind.*, 1906, **25**, 515) and reference to the results obtained will give the analyst some idea as to the nature of these reactions, and the absolute need for some artificial control over the absorption by hide powders under varying conditions. The figures given above represent the extreme errors possible with this process, for it was found that in the presence of tannic acid in the solution the hide powder was apparently not so readily hydrated. The portion dissolved from the hide powder and the absorption of gallic acid were both reduced. A modified hide powder must be looked for as a standard, which will give equal results to the above separation method when using gallic acid alone. It may then be assumed that in mixtures of tannic and gallic acids no absorption of the latter, or solution of the hide-powder substance will take place. Owing to this varying action a blank experiment with distilled water may be quite useless for determining the soluble matter in any sample of hide powder under the conditions of analysis and such a test should be discarded.

Only certain portions of the hide can be used in the preparation of hide powder, and all samples used are prepared under standard conditions and in bulk. From the foregoing considerations the empirical nature of this method of analysis is obvious.

The absorption of colouring or other substances by hide powder or gelatin may introduce a serious error as they may be weighed as tannin. The fact that these substances are absorbed under certain conditions by these precipitating media is one of real concern to the analyst, and must be considered when deciding on any method of

analysis. Where this disturbing influence is present a process should be selected which does not depend on the direct weighing of the separated tannic acid. In the case of the control of solutions, or vats in industrial operations this may be necessary. It may be advisable in such cases to assay the original tannin material by the hide-powder process, and also by the one selected for use in the dye house or tanning yard, so that the latter method may be standardised in terms of the hide-powder processes. The mere "carrying down" of other materials coloured or otherwise of an inactive nature by say a copper, or antimony lake need not necessarily interfere with the assay of the tannin where the resulting precipitate is not weighed.

The influence of third substances (such as acids or salts) on the proportion of gallic acid carried down, or absorbed by, the gelatin coagulum or hide powder may be both marked and definite in its nature.

In fact, gelatin nearly free from ash will not precipitate tannic acid (Weiske, *Zeit. f. Phys. Chem.*, 1891, **7**, 460) but on the addition of an electrolyte precipitation takes place. In the same way albumin free from inorganic salts will not coagulate under the action of heat.

It has been pointed out that these results and others obtained by Pauli (*Pfluger's Archiv.*, 1899, **78**, 315) show that slight variations in the conditions such as the varying presence of salts may materially alter the composition of the precipitated coagulum and emphasise the absolute need for an official or recognised method of analysis based upon conditions which will reduce these errors to a minimum, or at any rate standardise them (see J. T. Wood, *Collegium*, 1908, **337**, 494; also *J. Soc. Chem. Ind.*, 1908, **27**, 384).

The Oxidation Method of Tannin Assay.

This process, which was first worked out by Löwenthal, is based on the fact that tannin is oxidised in acid solutions by permanganate, though the slowness of the oxidation and the want of definition of the end-point render the method unsuitable without modification. By addition of a considerable quantity of indigo the oxidation of the tannin is controlled, and the end-point is rendered more definite. As solutions of commercial tannin-matters contain other oxidisable matters besides tannins, it is necessary to separate these and titrate a second time, in order to ascertain the volume of permanganate actually required by the tannin present. This separation may be effected by

digestion with hide powder, or by a solution of gelatin, the use of which was first suggested by Estcourt.

The compounds of gelatin and tannin have recently been studied by J. T. Wood (*Collegium*, 1908, **318**, 257 and **319**, 269) and reference to the results will show that the ratio of tannin to gelatin is not a constant, the tannin being precipitated in greater ratio in stronger solution. Washing also influences the ratio, it being in one case reduced from 310 to 212. The composition of the gelatin coagulum formed has been studied by Trunkel (*Biochem. Zeit.*, 1910, **26**, 458). It varies greatly according to the conditions of coagulation.

In practice, Löwenthal employed a mixed solution of gelatin and common salt, to which a small quantity of sulphuric or hydrochloric acid had been added. In using this form of the process it is generally necessary to let the mixture stand several hours in order to obtain a clear filtrate, besides which the gelatin substance remaining in solution has a slight though generally negligible reducing action on the permanganate. In some cases, even after long standing, filtration is very tedious, and it has also been proved by F. Simand (*J. Chem. Soc.*, 1883, **43**, 1237) that a certain proportion of the tannin-gelatin precipitate, varying with the acid and kind of tannin present, remains in solution, and hence that the results obtained by the process are below the truth.

On account of these objections to Löwenthal's process, Procter proposed a modification in which the excess of gelatin is removed by saturating the liquid with common salt, and the filtration is facilitated by addition of kaolin. A perfectly clear filtrate wholly free from tannin, and nearly so from gelatin, is thus obtained without difficulty. The following were the details given:

Ten grm. of sumac or valonia or 20 grm. of finely ground bark are exhausted by water (see page 57).

a. 5 c.c. of the solution for analysis is run into a porcelain basin and diluted to 750 c.c. by addition of distilled water and 20 c.c. added of an indigo solution, a litre of which contains 5 grm. of the purest indigo-carmine,[1] and 50 c.c. of concentrated sulphuric acid. A solution containing 1 grm. of potassium permanganate per litre is then run in very slowly drop by drop with vigorous stirring, until the liquid becomes transparent, when the addition is continued more

[1] The indigo-carmine (sodium sulphindigotate) must be of such quality that the solution when oxidised by permanganate is a pure yellow colour, free from a trace of brown or orange. Indigo-purple, which gives brown oxidation-products, interferes with the accuracy of the analysis. The indigo solution should be of such strength that 20 c.c., diluted to 750 c.c. with water, shall require from 14 to 16 c.c. of standard permanganate for its oxidation.

cautiously, with occasional pauses, until the clear yellow liquid appears of a faint pink colour on the margin. The titration is repeated, the volumes of permanganate required in the two cases being added together and called *a*.

In employing the oxidation-process, the volume of permanganate required by the tannin should *in no case* exceed 2/3 of that reduced by the indigo. If the result of the titration shows that this proportion has been exceeded, the experiments must be repeated with a smaller quantity of the tannin solution.

b. For the gelatin separation 50 c.c. of the tannin solution should be mixed in a flask with 28.6 c.c. of a freshly made and filtered soltuion of gelatin[1] (2 grm. per 100 c.c.). After shaking, the liquid is saturated with common salt,[2] which increases the volume to 90 c.c. 10 c.c. of dilute sulphuric acid (containing 1 volume of the concentrated acid in 10) should next be added, and then about 10 grm. of pure kaolin or barium sulphate. The flask should be vigourously shaken for a few minutes, and the liquid passed through a dry filter. This is effected rapidly, and the filtrate is perfectly clear. Two quantities of the filtrate of 10 c.c. each (= 5 c.c. of original infusion) are then treated with indigo solution, and titrated with standard permanganate as before, the result being called *b*. The difference $(a-b)$ between the volume of permanganate employed for the 2 quantities of unprecipitated tannin infusion (*a*), and that decolourised by the 2 portions of the filtrate, gives the volume of permanganate solution decolourised by the tannin in 10 c.c. of the original infusion.

c. 10 c.c. of an N/10 solution of oxalic acid (6.3 grm. of crystallised oxalic acid, $C_2H_2O_4 + 2H_2O$, per litre) are diluted with distilled water to about 500 c.c., warmed to about 60°, 20 c.c. of pure dilute sulphuric acid added, and standard permanganate run in with constant stirring till a pink colouration, remaining permanent for 1 minute, shows that oxidation is complete. The volume of permanganate consumed, which is called *c*, is evidently that required for the oxidation of 63 milligrm. of crystallised oxalic acid.

[1] 2 grm. weight of good gelatin is allowed to swell in distilled water for a few hours, then melted by immersing the flask in boiling water, and the resultant solution made up to 100 c.c.

[2] B. Hunt (*J. S. C. I.*, 1885, 4, 263) has indicated that the excessive quantity of salt recommended by Procter causes the precipitation of a notable quantity of gallic acid when much is present. Hence he prefers to mix 50 c.c. of the tannin solution with 25 c.c. of a 2% solution of gelatin, and then add 25 c.c. of a saturated solution of common salt containing 50 c.c. of strong sulphuric acid per litre. Kaolin is next added, and the mixture well agitated and filtered, and in all other respects Procter's method of operating is adhered to. Hunt's modification is approximately a return to Löwenthal's original method, and introduces its attendant error. In the presence of gallic acid the gelatin separation is a doubtful one in all cases.

The proportion $c : (a-b) = 63 : x$ will give the number of milligrm. of oxalic acid corresponding in reducing power to the tannin in 10 c.c. of the infusion assayed. If 10 grm. of the sample were extracted and the solution made up to 1 litre, 10 c.c. of the infusion represented 0.1 grm. of the tanning material, and hence the number of milligrm. of oxalic acid will be *the percentage of tannin expressed in terms of crystallised oxalic acid.* It is frequently convenient to express the results of the assay in this way, since what is required in practice is not the absolute weight of tannin in the various materials, but their *comparative* value in terms of tannin. It is impossible to express the results of tannin assays in actual percentage of tannin; unfortunately the different varieties of tannic acid have different reducing powers, and the expression of the results of the assay of oak-bark or cutch in terms of gallotannic acid would be misleading. The expression of assays of all kinds of tannin-matters is therefore made in terms of oxalic acid.[1]

The Yorkshire College method as given by Procter (Leather Industries Laboratory Book) varies in details from the others. It is given here and recommended for general use, when it is decided to employ this method.

(I) The solutions required are potassium permanganate 0.5 grm. per litre, freshly prepared if possible.

(II) Pure indigo carmine solution (potassium or sodium sulphindigotate) 5 grm., and concentrated H_2SO_4 5 grm. per litre. 25 c.c. of this solution should equal 30 c.c. of the permanganate.

(III) Solution of pure tannic acid, or gallic acid may be substituted on account of its purity.[2]

The tannic acid solution is never quite pure, and must be standardised by the hide-powder process. It must not show less than 90–95% tannic acid, and a correction must be made for this.

25 c.c. of the indigo carmine solution is mixed in a beaker with about 750 c.c. water, and the permanganate added drop by drop till a pure yellow colour is obtained. Care has to be taken to stir the solution in a constant and regular way. The titration is then repeated in the pres-

[1] Von Schroeder has suggested the use as a standard of commercial gallotannic acid, the moisture in which has been determined by drying at 95°. and which has been proved to contain not more than 5% of non-tannin matters unprecipitable by hide or gelatin; dividing the result obtained by 1.05 to allow for the slightly higher reducing power of the impure tannin. Procter has proposed to employ gallic acid for standardising the permanganate, as it is readily obtained pure, and is oxidised in presence of indigo in a manner very similar to gallotannic acid.

[2] The copper process with the lead separation (see page 70) might however be used to estimate the gallic acid present in the pure tannic acid (III) as a possible alternative to this method. There seems no real reason, however, why gallic acid should not be used, as it is readily obtained in a pure state.

ence of 5 c.c. of the tannic acid solution, or the tannin solution under examination. These figures give the total astringent present in terms of tannic acid. To obtain the astringent taken up by hide powder, which may be less than that estimated by the permanganate, the usual hide-powder separation (see page 71) may be adopted.

The gelatin separation method may be used where the proportion of gallic acid is small.

Hunt's modification being selected for use.

Solutions required

(1) Pure gelatin, 2 grm. per 100 c.c.

(2) Saturated solution of sodium chloride containing 50 c.c. sulphuric acid per litre.

To 50 c.c. of the tannin solution is added 15 c.c. of gelatin, 25 c.c. of the salt solution and about a teaspoonful of kaolin, and the whole is well shaken for 5 minutes and filtered. Double the original volume taken for titration is used for titration.

The actual reduction-equivalents of the different kinds of tannin are imperfectly known, and the greatest caution must be observed in their use. Neubauer states that of gall-tannin as 41.57; that is 41.57 grm. of gall-tannin possess the same reducing power on permanganate that is possessed by 63 grm. of crystallised oxalic acid ($C_2H_2O_4.2H_2O$), or 56 grm. of iron in the ferrous state, or that 41.57 grm. of gall-tannin decolourise a volume of permanganate solution yielding 8 grm. of available oxygen. Neubauer's equivalent for gallotannic acid has been confirmed by Ishikawa (*Chem. News*, 1888, **42**, 274), who found 41.688 as the figure for the tannin of *Kibushi*, or Japanese gall-nuts. Councler and von Schroeder, on the other hand, find the equivalent to be only 34.25.[1] For oak-bark tannin, Neubauer gives the equivalent 62.36, which is confirmed by Oser's figure, 62.35, and approximately by that of Simand, 61.1. The reduction-equivalents of other varieties of tannin are uncertain. Oser's and Neubauer's figures for oak-bark tannin show a reducing power nearly identical with that of oxalic acid (=63), and hence the results of the titration may be conveniently expressed in terms of oxalic acid. An alternative plan is to state the strength of the tannin-matter in terms of

[1] This discrepancy has been shown by von Schroeder to be due to the different manner in which the permanganate was added in the titration, Neubauer employing the "drop method," while Councler and von Schroeder added the solution in successive quantities of 1 c.c. with a short interval between each addition. This modification seriously affects the volume of the standard solution required. It is clear that by expressing such results in figures showing the second or third decimal places, authors show a lack of appreciation of the probable error of the method.

"oxygen consumed." Each 1 c.c. of a solution of potassium permanganate (containing 1 grm. of the salt per litre) which may have been decolourised by the tannin, represents 0.000253 of "oxygen consumed," or 0.00199 (practically 0.002) grm. of crystallised oxalic acid. Neubauer's equivalent for gall-tannin is practically two-thirds of the bark and oxalic acid figures. The first figure is applicable to galls, and probably to divi-divi, sumac, and myrabolans; the second to oak-barks, and probably to oak-wood, valonia, chestnut extract, etc. Gallic acid consumes a greater volume of permanganate than the tannin from which it is derived. Hence, as commercial tannin is often largely contaminated with gallic acid, it not unfrequently shows over 100% of tannin when assayed.[1]

This method (Löwenthal) has been criticised by Procter and Hirst (*Collegium*, 1909, **361**, 193). The non-tannins in the case of gelatin precipitation are too high though they are approached, or even exceeded in some cases, by the unchromed hide-powder (shaking) method. When chromed powders are used the results are invariably lower. Paessler's lightly chromed powder (dry) is said to be equally suitable to the official powder (chromed) for the Löwenthal method or to the Kopecky air dried chrome leather machine shavings. In testing the tannin liquors 7 grm. of the dry powder are taken, and a little kaolin added to 100 c.c. of the liquor. This is well mixed by hand shaking, and then by 10–15 minutes in a shaking machine. After passing through filter-paper until clear 5 c.c. are taken, 20 c.c. of indigo added, and titrated with the permanganate solution. The latter is titrated against a standard gallic acid solution, and the results expressed "in terms of gallic acid." The estimation of the non-tannins has also been the subject of a special study by H. R. Zeuthen (*Collegium*, 1908, **326**, 366).

According to Cech, no interference in the estimation of tannin by permanganate is produced by the presence of acetic acid, citric acid, tartaric acid, malic acid, cane-sugar, dextrin, gum, fat, caffeine, or carbamide, provided the solution be diluted as directed.

The permanganate and possibly all other processes for the assay of tannin-matters are merely comparative, and give results useful only as a means of comparing the qualities of samples of material of the same character. Thus, bark may be compared with bark, and valonia with valonia, and so on, but *all cross comparisons are impossible.* Even if

[1] Mixtures of tannins with gallic acid cannot be directly estimated by the volumetric process, for 1 grm. of the dry acid reacts with the same quantity of permanganate as 1.505 grm. of dry tannin.

the exact percentage of tannin could be calculated, the practical and commercial value of tannin materials does not depend on the quantity of tannin only, but on the colour, weight and quality of the leather produced, though the same process should give results of approximate accuracy when applied to different materials containing the same variety of tannin.

P. Sisley (*Bull. Soc. Chim.* [3], 9, 755) precipitates the tannin as a zinc salt, and oxidises the latter with permanganate. An ammoniacal solution of zinc acetate is used for the precipitation, made by dissolving 40 grm. zinc oxide in hot, dilute acetic acid (65 c.c. glacial acid and 50 c.c. water), and adding excess of ammonia. The tannin solution is treated with zinc solution, and the precipitated zinc compound rapidly filtered and washed with dilute ammonia. In this way the gallic acid and other impurities are removed. The precipitate is then washed into a porcelain basin and titrated with potassium permanganate.

The following figures given by Procter show the results to be expected when applying the permanganate process to the assay of various tannin-matters. The estimations were made by the method described on page 63.

	In terms of oxalic acid	
	Tannin	Other oxidisable substances
Valonia; good Smyrna	29.1 %	2.3 %
Valonia; good Smyrna	30.7 %	2.1 %
Valonia; good Smyrna	30.5 %	1.9 %
Valonia; good Smyrna	32.6 %	2.7 %
Hungarian larch extract	14.78%	1.95%
Hungarian larch extract	18.08%	2.33%
Chestnut-wood extract (sp. gr. 1.205)	25.53%	3.68%
Pegu cutch	63.59%	2.45%
Spent liquor.[1]	0.12%	11.0 %

The permanganate process has been applied by A. Hill to the estimation of tannin in *tea* (*Analyst*, 1881, 6, 95). The average proportion of tannin, in terms of oxalic acid, found in the 32 samples of tea examined was 14.8 %, the extreme results being 6.18 in black Assam tea and 26.90 in a black caper tea. Other determinations of

[1] The results of the assay of the spent liquor are instructive. The liquor originally contained from 10 to 15% of the tannins from oak-bark, valonia, myrabolans, gambier, hemlock, etc., which after contact with hide was reduced to the small proportion of 0.12%. That a portion had not been absorbed but decomposed is shown by the large accumulation of oxidisable impurities (equal to 11% of oxalic acid). Spent liquors are generally very pale in colour, as also are the filtrates from the gelatin precipitation, a fact that indicates that the colouring matters present in tannin materials resemble tannin in their behaviour to both hide and gelatin, being carried down by the coagulum in the latter case.

the proportion of tannin in tea have been made by O. Kellner (*Landw-Versuchs Stat.*, 1886, 370) and J. F. Geisler (*Analyst*, 1884, 9, 220) (see also page 88).

The following figures, due to B.Hunt (*J. Soc. Chem. Ind.*, 1885, 4, 264), show the insoluble matter and total extract of various commercial tannin materials, and the oxalic acid equivalents of the total oxidisable matters, and of the tannin as precipitated by Procter's and Hunt's methods.[1] The difference between the results obtained by these 2 methods was attributed by Hunt to the precipitation of gallic acid by the excess of salt solution employed by Procter.

Material	Insoluble matter	Total extract	In terms of oxalic acid		
			Total oxidisable matters	Tannin, Procter	Tannin, Hunt
"Pure tannin,"	....	....	135.76	122.44	121.93
English oak-bark	66.15	18.38	15.70	13.54	11.97
Canadian hemlock-bark	75.25	13.96	9.03	7.46	7.08
Larch-bark	60.80	20.64	8.20	7.17	6.15
Mangrove-bark	49.70	26.60	31.35	29.71	28.48
Alder-bark	68.00	19.36	8.27	6.15	5.73
Valonia	46.05	38.50	37.41	35.24	30.50
Myrabolans	....	42.80	48.23	38.43	38.00
Sumac	47.77	44.10	42.53	34.30	31.46
Turkish blue galls	36.35	48.40	73.38	65.83	59.96
Aleppo galls	14.32	68.80	98.85	87.82	83.05
Wild galls	54.17	31.70	26.21	18.75	16.56
Divi-divi	29.90	54.38	66.68	62.62	61.22
Pomegranate rind	49.50	41.00	27.58	24.18	23.12
Tormentil root	67.95	19.70	22.27	20.98	20.68
Ratanhy root	66.00	18.80	22.27	20.15	19.30
Pure Indian tea	53.40	34.46	23.06	18.65	17.40
Pure China tea	62.60	24.50	18.03	14.21	14.09
Cutch	4.75	61.60	57.65	51.95	44.24
Gum kino	1.00	79.30	66.39	59.55	51.55
Hemlock extract	....	48.78	35.16	33.17	30.98
Oak-wood extract	....	37.78	33.49	26.90	23.86
Chestnut extract	....	50.28	39.77	32.63	28.88
Quebracho extract	....	49.00	48.22	44.45	40.84
Tan-liquor (sp. gr. 1.030)	....	6.01	4.84	3.14	2.10
Spent liquor (sp. gr. 1.0165)	....	3.10	1.40	0.37	0.25

[1] Hunt stated in the same paper that treatment with gelatin and salt does not remove all that is of tanning value from solutions of gambier and allied materials, hence he recomemended the removal of the tannin in such cases by means of purified skin-shavings. These he added in the proportion of 5 grm. to 100 c.c. of a 1% gambier solution, and after 12 hours filtered and titrated the filtrate with permanganate in the usual way. The following results were obtained:

	Insoluble matter	Total extract	In terms of oxalic acid	
			Total oxidisable matter	Absorbed by skin
Cube gambier	5.31	74.40	70.12	51.07
Sarawak gambier	3.67	70.70	63.13	47.09
Bale gambier	1.40	63.54	56.00	43.70

The permanganate process of determining tannin was some years ago submitted to examination by a commission of German chemists. After reviewing earlier methods they recommended the following modifications of the permanganate process for general adoption: 1. That the *permanganate* solution contain 10 grm. of $KMnO_4$ in 6000 c.c. 2. That the *indigo-solution* should be made by dissolving 30 grm. of air-dry sodium sulphindigotate in 3000 c.c. of dilute sulphuric acid (1 : 3), 3000 c.c. of water being added, and the whole shaken till dissolved, and the liquid filtered. 20 c.c. of this solution in 750 c.c. of water should be used in each titration, and should reduce about 10.7 c.c. of the permanganate solution. 3. *Hide powder* was substituted for the ordinary gelatin solution, and was to be light coloured and in a fine woolly state of division, yielding to cold water no substance capable of reducing permanganate.

Instead of adding the permanganate solution drop by drop, the commission recommended (with very doubtful advantage) that an addition be made of 1 c.c. at a time, and the mixture vigorously stirred for 5 or 10 seconds after each addition. As soon as the liquid has become bright green, 2 or 3 drops at a time should be cautiously added with stirring, till the liquid is pure yellow. The results obtained by the "1 c.c. method" differ considerably from those obtained by the ordinary or "drop method," which was that employed by Neubauer and Oser for the determination of the reduction co-efficients of tannins. It has, however, been shown by H. R. Procter (*J. Soc. Chem. Ind.*, 1886, **5**, 79) that the results are more influenced by the rapidity of mixing than by subsequent time of standing, and that the 1 c.c. method, while it gives a higher consumption of permanganate than the drop method, is more affected by variations in stirring.[1]

E. B. (*Zeit. Anal. Chem.*, 1886, **26**, 680) suggests the use of ferric acetate instead of gelatin for precipitating tannin. The process has been tried on gall-tannin, and F. Gantter (*J. Chem. Soc.*, **54**,) does not confirm its accuracy in this case.

Other investigators have recommended the use of an ammoniacal

1 Procter points out that the limit of the action is not a complete oxidation of the organic matter, but only a partial one of the bodies more readily oxidisable than indigo; and hence toward the end of the operation, when little indigo remains, the permanganate is partially consumed in further oxidising the products of the normal reaction; and that this is least the case when the permanganate is added slowly and rapidly mixed with the liquid, so as to bring it into immediate contact with the remaining indigo. Procter obtained very uniform results by the use of a stirrer consisting of a perforated porcelain disc, which was worked up and down in the beaker by means of an attached glass rod. He used a capillary jet to the point of the burette, allowing the permanganate to run in steadily through out the titration.

solution of copper for removing the tannin. This is not capable of universal application. *Sumac* may be precipitated by ammonio-cupric acetate,[1] titrating of the solution by permanganate and indigo before and after the treatment.[2]

N. H. Darton (*J. Amer. Chem. Soc.*, 1882, 4, 4) employed copper ammonio-sulphate in the following manner: 20 grm. of *hemlock-bark*, or an equivalent amount of other tannin material, are extracted first with cold and then with several quantities of boiling water. The mixed infusions are treated with 25 c.c. of dilute sulphuric acid (1 : 10), the liquid filtered, and the filtrate rendered slightly alakline with ammonia, any precipitate being filtered off. A further quantity of 25 c.c. of dilute sulphuric acid is then added, and the liquid made up to 1 litre. 100 c.c. of this solution is treated with an equal measure of a solution of cupric sulphate (containing 1.25% of the salt), to which sufficient ammonia has been added to dissolve the precipitate first formed. The solution is passed through a dry filter, and a definite measure of the filtrate neutralised and titrated for "not tannin" with indigo and permanganate in the usual way. Procter stated that the preliminary treatment with acid and ammonia is unnecessary in the case of *valonia* (and probably in that of oak-bark), and that the process gave results practically identical with the then improved gelatin method, while it is much less troublesome. With *chestnut extract* the results were claimed to be satisfactory, provided the preliminary treatment be omitted, as this removes 75% of the matter precipitable by gelatin, and cutch behaves similarly. On the other hand, a sample of *larch extract*, which tanned well and showed 18% of tannin by the gelatin method, gave *no* precipitate with the ammonio-cupric solution. This peculiarity would allow of the estimation of valonia-tannin in presence of larch-tannin, and the same principle is utilised in other cases (see page 70).

When applicable, the copper process has the advantage that the precipitate may be washed with a solution of ammonium carbonate,

1 Meyer (*Chem. Zeit.*, 1890, 14, 1202) says that the precipitation with copper acetate yields excellent results if the precipitation takes place in a hot solution, and washing with hot water follows immediately. The precipitate is dried at 110°, weighed, and ignited to CuO. From the weight of the total precipitate, four-fifths of the weight of the resulting copper oxide is deducted, which gives the total tannin. This ignition might be saved by estimating the amount of copper required volumetrically and using this same amount in the precipitation.

2 By this process, I. Macagno (*Chem. News*, 1880; 41, 63) found that the upper side of sumac leaves was considerably richer in tannin than the lower, the proportion in old leaves being less than in young. The results varied from 8.77% of tannin in the lower side of old, to 25.82% in the upper side of young leaves.

dried, and weighed.[1] Or the precipitate may be ignited, the residue moistened with nitric acid, and re-ignited, and the cupric oxide weighed. Its weight, subtracted from the weight of the precipitate previously found, gives that of the tannic acid with which it was combined, or the latter may be found by multiplying the weight of CuO by 1.034. This factor probably applies only to gallotannic acid.

Dreaper (*Chem. News*, 1904, **90**, 111) gives the latest details for his volumetric copper process. Standard solutions containing (1) copper sulphate equivalent to 0.05 CuO per c.c., (2) 20 grm. lead acetate and 60 c.c. glacial acetic acid per litre, and (3) 50 grm. ammonium carbonate and 50 grm. sodium sulphite per litre are required.

(*a*) 50 c.c. of the tannin solution (containing 10 to 15 grm. per litre) is titrated with the copper solution after heating to 80° to 90° for a few minutes with excess of $CaCO_3$ (about 1 to 2 grm.) and cooling. The result in terms of CuO represents the total tannin and gallic acid, and any "non-tannins" which precipitate copper salts, but not the non-tannins which may be carried down mechanically.

(*b*) A second 50 c.c. is taken and 10 c.c. of the lead solution added in the presence of barium sulphate. It is well shaken and after 5 minutes the lead tannin precipitate is filtered off through dry filter-paper, 0.5 grm. sodium sulphate (anhydrous) is added and after 5 minutes the lead sulphate is filtered off. 40 c.c. of the filtrate is taken and titrated as in (*a*). The result gives the non-tannins precipitated by copper salts (gallic acid), and when subtracted from (*a*) gives the tannins also.

(*c*) 50 c.c. of tannin solution is taken and 25 c.c. of No. 3 solution added. The copper tannate formed on titrating this solution in the cold is free from gallic acid but only the tannic acids insoluble in ammonium carbonate are precipitated, so that a comparison with the results obtained in (*b*) indicates the amounts of total tannic acid, the two groups of tannic acids, and gallic acid and the non-tannins which may form compounds with copper, respectively. It is generally sufficient in practice to use only the lead separation which entirely removes all tannins but no gallic acid.

The end-point is obtained in all cases by removing a drop of the solution on a glass rod and pressing it into a doubled sheet of good filter-paper (*e. g.*, C. S. & S., No. 589, No. 3 brand). The under sheet

1 Dreaper recommends the precipitation in the presence of sodium sulphite to prevent oxidation (*Chem. News*, 1904, 90, 111).

will be then wetted with the filtered solution. A drop of ferrocyanide of potassium solution placed on this will show a pink colouration with an excess of copper. When testing the (*c*) solution in this way the ferrocyanide must be strongly acid with acetic acid, and the final result must be confirmed after an interval of 3 minutes, as the copper salt is precipitated slowly in this case. The process has been used to detect errors in the hide powder and "collin" processes. It gives the mordant value of any tannin and is not affected by any "non-tannins" or colouring matter carried down mechanically, or by free acid in the liquors. The presence of reducing sugars has no influence on the results.

EUROPEAN OFFICIAL METHOD OF TESTING TANNIN MATERIALS. (I. A. L. T. C.)

General Conditions.

Corrected up to 1910 this method stands as follows:

I.—**The solution for analysis** must contain between 3.5 and 4.5 grm. of tannin matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50°, but if the Teas extractor be used the first portion of the extract shall be removed from the influence of heat as soon as possible.

II.—**The total solubles** must be estimated by the evaporation of a measured quantity of the solution previously filtered until optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker placed in a good light on black glass or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution a correction must be ascertained and applied as decsribed in Section VI. Filtration shall take place between the temperatures of 15° and 20°. Evaporation to dryness shall take place between 98.5° and 100° in shallow flat-bottomed basins which shall afterwards be dried until constant at the same temperature and cooled before weighing for at least 20 minutes in air-tight desiccators over dry calcium chloride.

III.—**The total solids** must be estimated by drying a weighed portion of the material, or a measured portion of its uniform turbid solution at a temperature between 98.5° and 100° in shallow flat-bottomed basins which shall afterwards be dried till constant at the same temperature and cooled before weighing for not less than 20 minutes in an air-tight desiccator over dry calcium chloride. "*Moisture*" is the difference between 100 and the percentage of total solids and "*Insoluble matter,*" the difference between the total solids and total solubles.

IV. **Non-tannins.**—The solution must be detannised by shaking with chromed hide powder till no turbidity or opalescence can be produced in a clear solution by salted gelatin. The chromed powder must be added in one quantity equal to 6.0 to 6.5 grm. of dry hide powder per 100 c.c. of tanning solution and must contain not less than 0.2 and not more than 1% of chromium reckoned on the dry weight and must be so washed that in a blank experiment with distilled water not more than 5 mgrm. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder shall be estimated and allowed for as water of dilution.

V. **Preparation of the Infusion.**—Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 grm. of tannin per litre, and not more than 4.5 grm. or less than 3.5 grm. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask filled up to the mark with boiling water, and well mixed and rapidly cooled to a temperature of 14.50° and accurately made up to the mark again, well mixed and filtered at once. Sumac and myrabolans extracts should be dissolved at a low temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask and the undissolved portions being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials, previously ground till they will pass through a mesh of 5 wires to the cm., are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50°, and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours

before commencing the percolation which should occupy not less than 3 hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately, as "*difficultly soluble substances.*" The liquid in the flask must after cooling be accurately made up to 1 litre.

VI. **Filtration.**—The infusion shall be filtered till optically clear to both transmitted and reflected light (see Section 11). No correction for absorption is needed with the Berkfeld candle, or for S. & S. 590 paper if a sufficient quantity (250–300 c.c.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed the average correction necessary must be ascertained in the following manner: About 500 c.c. of the same or a similar tanning solution is filtered perfectly clear and after thorough mixing 50 c.c. is evaporated to determine "total soluble No. 1." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible) and 50 c.c. is evaporated to estimate "total soluble No. 2." The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of estimating correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkfeld candle till optically clear by rejecting the first 300–400 c.c. and returning the remaining filtrate repeatedly, and at the same time to evaporate 50 c.c. of the clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

VII. **Detannisation.**—The hide powder used shall be of fibrous texture, thoroughly delimed, preferably with hydrochloric acid, shall not require more than 5 c.c. or less than 2.5 c.c. of N/10 NaOH or KOH to produce a permanent pink with phenolphthalein on 6.5 grm. of the dry powder suspended in water. If the acidity does not fall within these limits it must be corrected by soaking the powder before chroming for 20 minutes in 10 to 12 times its weight of water to

Note. It is obvious that an average correction must be obtained from at least 5 estimations. It will be found that this is approximately constant for all materials and amounts in the case of S. & S. 605, 150 c.c. being rejected, to about 5 milligrm. per 50 c.c. and when 2 grm. of kaolin are employed in addition, to 7.5 milligrm. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.

which the required calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70–75% of water and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 grm. per 100 c.c. The powder when sent out from the makers shall not contain more than 14% of moisture and shall be sent out in air-tight tins.

The detannisation shall be conducted in the following manner: The moisture in the air-dried powder is estimated and the quantity equal to 6.5 grm. actual dry hide powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made and wetted again with approximately 10 times its weight of distilled water. 2 grm. per 100 of dry powder of crystallized chromic chloride ($Cr_2Cl_6.12H_2O$) (Kahlbaum) is now dissolved in water and made basic with 0.6 grm. Na_2CO_3 by the gradual addition of 11.25 c.c. of N/1 solution, thus making the salt correspond with the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder and the whole churned slowly for 1 hour. In laboratories where analyses are continually being made it is more convenient to use a 10% stock solution, made by dissolving 100 grm. of $Cr_2Cl_6.12H_2O$ in a little distilled water in a litre flask, and very slowly adding a solution containing 30 grm. of anhydrous sodium carbonate with constant stirring, finally making up to the mark with distilled water and well mixing. Of this solution 20 c.c. per 100 grm. or 1.3 c.c. per 6.5 grm. of dry powder should be used.

At the end of 1 hour the powder is freed as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water until on adding to the filtrate 1 drop of 10% K_2CrO_4 and 4 drops N/10 $AgNO_3$ a brick-red colour appears. 4 or 5 squeezings are generally sufficient. Such a filtrate cannot contain more than 0.001 grm. of NaCl in 50 c.c.

Very woolly powders require slightly more than 10 times the weight. A powder may be considered "woolly" if it cannot be poured out like sand from a beaker (Procter).

The powder is then squeezed to contain 70–75% water, and the whole weighed. The quantity Q containing 6.5 grm. dry hide is thus found, weighed out, and added immediately to 100 c.c. of the unfiltered

tannin infusion along with 26.5 Q of distilled water. The whole is corked up and agitated for 15 minutes in a bottle rotating at not less than 60 revolutions per minute. It is then squeezed immediately through linen, 1 grm. of kaolin added to the filtrate, and the latter stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c., or the residue of 50 c.c. is multiplied by 6/5. The non-tannin filtrate must give ho turbidity with a drop of a 1% gelatin 10% salt solution. 1 grm. of kaolin, free from solubles, must be used either by mixing it with the hide powder in the shaking bottle, or with the liquid before filtration.

VIII. **Analysis of Used Liquors and Spent Tans.**—These shall be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being diluted or concentrated *in vacuo*, or in a vessel so closed as to restrict access of air, until the tanning matter lies, if possible, between 3.5 and 4.5 grm. per litre, in no case exceeding a concentration of 10 grm. per litre of total solids; the weight of hide powder used shall not be varied from 6.5 grm.

The results shall be reported as shown by the direct estimation, but it is desirable that, in addition, efforts shall be made by the estimation of acids in the original solution and in the non-tannins in residues, to ascertain the amount of lactic acid and other non-volatile acids absorbed by the hide powder and hence returned as "tannin matters." In the case of tans it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrary assumed percentage of water, and in that of liquors whether the percentage given refers to weight, or to grm. per 100 c.c.; in both cases the sp. gr. shall be reported.

IX. All evaporation shall be rapidly conducted at steam temperature in shallow flat-bottomed basins of not less than 6.5 cm. diameter, to apparent dryness, and shall be subsequently dried between 98.5° and 100° in a water or steam-oven until of constant weight, and shall be afterward cooled in small air-tight desiccators over dry calcium chloride for at least 20 minutes and then weighed rapidly. Not more than 2 basins shall be placed in 1 desiccator and the basins must not be wiped after removal from the desiccator.

NOTE.—It was decided at the I. A. L. T. C. conference of 1908, that any method conforming to the conditions of Sections 1–4 may be regarded as conforming to the regulations, but that members of the

Association must work according to the detailed directions contained in Sections 5–8.

In connection with this paragraph the Reed-Alsop evaporator was strongly recommended, as also the Moeslinger drying oven, and the vacuum oven. The great inaccuracies caused by using ordinary air drying were pointed out. No restrictions are at present in force concerning the exact size and shape or composition of the basins.

Certain restrictions are imposed upon members of the I. A. L. T. C. and all analyses must be the average of duplicate determinations which must agree in the case of liquid extracts to within 0.60%, and in the case of solid extracts to within 1.5%.

Official Method of the American Leather Chemists' Association.

The official method of the American Leather Chemists' Association for 1911 differs in some respects from the I. A. L. T. C. method and the particulars are given here.

I. Crude Materials.

1. **Moisture Estimation.**—Upon receipt of the sample grind promptly and dry 10 grm. in the manner and for the period specified for evaporation and drying in extract analysis.

2. **Preparation of Sample for Extractions.**—Sample must be dried at a temperature not exceeding 60° and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

3. **Amount of Sample and Proportion of Water for Extraction.**—For fresh materials the amount of sample and proportion of water for extraction should be such as to give between 0.35–0.45 grm. tannin per 100 c.c. of solution. For spent materials this proportion should be approximated as closely as practicable.

4. **Extraction of Sample.**—Extraction should be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued till a portion tested with gelatin-salt solution fails to give a precipitate. At least 500 c.c. of the first portions of extracted solution should be removed and not subject to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

4*a*. **Sumac and Kindred Materials.**—Put the material (the amount should be such as to give between 0.35–0.45 grm. tannin per 100 c.c.

solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water and allow it to soak for an hour, then extract by collecting 2,000 c.c. of the extractive solution outside through lower tube in from six to eight hours. Let the extractive solution stand over night and analyse the following day by the official method for extracts.

5. **Analysis.**—After extraction and dilution solutions must be heated to 80° and analysis conducted as per official method for extracts. In the case of weaker dilutions than the official method specifies, the amount of hide powder must be reduced in proportion to the tannin. 10 grm. of the air-dried sample should be dried as in 1. to determine moisture content of the portion extracted, and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

II. Analysis of Extracts.

6. **Amount and Dilution for Analysis.**—Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35–0.45 grm. tannin per 100 c.c. of solution; dissolve in exactly 900 c.c. of distilled water at 80°, and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not fall below 20°.

7. **Total Solids.**—Thoroughly mix solution, pipette 100 c.c. into tared dish, evaporate and dry as directed under "*Evaporation and Drying*."

8. **Soluble Solids.**—To 1 grm. of kaolin in a beaker add 75 c.c. of solution. Stir and pour on a 590 S. & S. 15 cm. pleated filter-paper, return filtrate to paper for 1 hour keeping filter full. Then pour solution from filter, or remove with pipette. Bring 800 c.c. of solution to 20°, refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as the solution comes *clear*. Keep filter full. Evaporate and dry the first 100 c.c. of filtrate, as under "*Evaporation and Drying.*" Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

9. **Non-tannins.**—A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with 25 times its weight of water till thoroughly soaked. Add 3% of chrome alum in solution. Agitate by either

shaking or stirring occasionally for several hours and leave over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide using a press if necessary, so that the wet hide will contain between 70 and 75% of moisture. Use approximately 20 grm. of wet hide for moisture estimation. Add to 200 c.c. of the original solution such quantity of the wet hide as represents from 12 to 13 grm. dry hide. Shake for 10 minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grm. of kaolin to the filtrate, stir and filter through folded filter (No. 1 F. Swedish recommended) of size sufficient to hold entire filtrate, returning till clear. Evaporate 100 c.c. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

The non-tannin filtrate must not give a precipitate with a 1% gelatin. 10% salt solution.

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the aid-dried powder and calculate the quantity equal to 12.5 grm. of the actual dry powder. Take any multiple of this quantity according to the number of analyses to be made and after chroming and washing as directed, squeeze to a weight representing 70–57% water. Weigh the whole amount and divide by the multiple of 12.5 grm. taken to obtain the weight of hide powder for 200 c.c. solution.

10. **Tannin.**—The tannin content is shown by the difference between the soluble solids and the corrected non-tannins.

III. Analysis of Liquors.

11. **Dilution.**—Liquors must be diluted for analysis so as to give as nearly as possible 0.7 grm. solids per 100 c.c. of solution.

12. **Total Solids.**—To be estimated as in *Extract Analysis.*

13. **Soluble Solids.**—To be estimated as in *Extract Analysis.*

14. **Non-tannins.**—To be estimated by shaking 200 c.c. of solution with the amount of wet chromed hide powder containing 70–75% moisture, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 c.c.	Dry hide powder per 100 c.c.
0.35–0.45 grm.	9–11 grm.
0.25–0.35 grm.	6.5–9 grm.
0.15–0.25 grm.	4–6.5 grm.
0.00–0.15 grm.	0–4 grm.

Solutions to be shaken for non-tannins as in *Extract Analysis*. 100 c.c. must be evaporated as in *Extract Analysis*.

IV. Evaporation and Drying.

15. **Evaporation and Temperature.**—All evaporations and dryings shall be conducted in the form of apparatus known as the "*combined evaporator and dryer*" at a temperature not less than 98°. The time of evapporation and drying shall be 16 hours.

16. **Dishes.**—The dishes used for evaporation and drying of all residues shall be flat-bottom glass dishes of not less than 2 3/4 in. diameter, nor greater than 3 in. in diameter.

Provisional methods for sampling tannin materials have been adopted by the American Association under 8 different headings (*J. Am. Leather Chem. Assoc.*, 1911, 7) which cover the details under which liquid extracts in barrels, liquid extracts in bulk, liquid extracts in tank cars, solid extracts, crude tannin materials, crude tannin materials in bulk, spent tan and woods, ground barks and cut woods, and liquid samples shall be taken, and if the analysis is required to conform with the U. S. A. official method care must be taken also to collect the samples under the conditions laid down from time to time by this association.

Notes on the Official Methods.—The American method of standardising hide powder is given by Procter as follows: Sufficient powder is weighed into an agitation flask for the work in hand to equal 6.5 grm. dry hide powder per analysis, acidity 8° (this being the natural acidity of the American powder); 10 times the weight of powder, in water, is then measured out, and such a quantity of N/10 NaOH is added as will reduce the bulk of the hide powder to an acidity of 5° (or 3 c.c. per 6.5 grm. powder) after mixing. The solution is poured on the powder, and the whole agitated for 20 minutes, and the required quantity of basic chromium chloride is added directly to the powder. The whole is agitated for 1 hour and proceeded with as usual (*Collegium*, 1908, **310**, 166). This is claimed to be superior in its working to the Paessler powder as used in Europe.

The Berkefeld candle was first recommended by Parker and Payne for the purpose of filtration of tannin infusions. It has met with official recognition (*Collegium*, 1904, 249).

The Reed method of filtration is conducted under reduced pressure

through asbestos and kaolin on the filter plate of a porcelain funnel (in one piece) of 2 1/2 in. diameter. 2 grm. of pure acid-washed asbestos of woolly texture are stirred with about 50 c.c. of the tannin solution and the mixture is then thrown on the filter plate and sucked down firmly on the plate by means of the vacuum; 2 grm. of kaolin are then stirred with 50 c.c. of the solution and, the vacuum being still

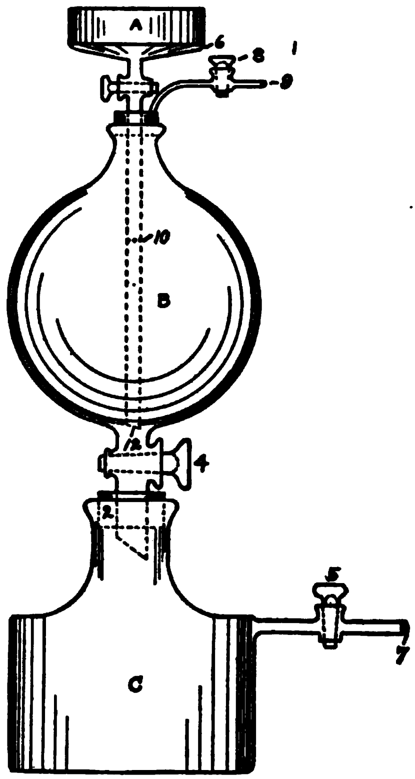


FIG. 2.—Apparatus for filtration of tannin solution.

on, poured gently on the asbestos layer. When the filtrate passes through clear, it is collected for analysis.

The apparatus shown in Fig. 2 is well suited for the purpose in question, the clear filtrate only being collected in B when it is running clear into C. Results indicate that as compared with the international official method, using No. 590 S. & S. paper or the Berkfeld

candle, a much clearer filtrate is obtained with less trouble. The results are tabulated and given in the *J. Am. Leather Chem. Assoc.* (1907, **2**, 420) and *Collegium* (1907, **285**, 414). Although there is a possible absorption of tannin by the asbestos and kaolin due to surface concentration the effect of this is not so great as with cellulose (filter-paper). It would seem that this method promises to be very useful in the future.

The Reed method has been further reported on (*J. Am. Leather Chem. Assoc.*, 1910, **5**, 179) and greater experience in its working will be necessary before it can be passed as equal to the Berkfeld candle method. When working with quebracho or hemlock bark this filter is said to be very satisfactory.

As a result of further use, Reed's method has been considered satisfactory by Procter (*Collegium*, 1910, 341).

The American Leather Chemists' Association decided (*J. Amer. Leather Chem. Assoc.*, 1909, **4**, 310–322) that the official method of chroming hide powder shall remain unaltered, but that the ratio of weight of water to hide powder used should be reduced from 25 to 10. The acidity of the hide powder should be adjusted so that 10 grm. require 10 c.c. N/10 NaOH for neutralisation, Houghs' method being used. They also recommend that extra care be taken to eliminate the error due to rapid cooling of quebracho and hemlock extracts, and to standardise the amount of insoluble matter precipitated which is affected by variations in such treatment.

The **United States of America Department of Agriculture** through the Bureau of Chemistry (*Bull.* No. 107, 1907) gives the Official and Provisional Methods adopted by the Association of Official Agricultural chemists. This does not differ in any material respect from the American Official method and is obviously founded on it.

The determination of acidity in hide powder has been criticised by D. L. Tucker (*J. Amer. Leather Chem. Assoc.*, 1909, **4**, 323–326). Comparing the 4 methods in use, viz., that of Bennett (*J. Soc. Chem. Ind.*, 1907, **26**, 456), Small (*J. Amer. Leather Chem. Assoc.*, 1907, **2**, 347; 1908, **3**, 75), Hough (*J. Soc. Chem. Ind.*, 1909, **28**, 804), and a modified Bennett method, Tucker finds difficulty in working them, the Hough method being considered the most accurate, but having a possible error equivalent to 0.2 c.c. of N/10 alkali.

The influence of the proportion of chromium in the present standard chromed hide powder on the analysis of oakwood extract has been

studied by J. Jedlicka (*Collegium*, 1908, **325**, 334) and the variations recorded when the chromium varies between 0 and 1% in the resulting hide powder. The results show variations in absorption amounting to 2.4%; between 0.1%–0.4% Cr. up to 1.1%; and between 0.4–1% Cr. to 1.4%. The need of a standard for the amount of chromium present is made evident.

Chroming of Hide Powder.—A new and more rapid method has been proposed in the place of the American Official method (*J. Amer. Leather Chem. Assoc.*, 1910, **5**, 419) by a committee appointed to report on the matter. The hide powder is wetted with ten times its weight of water and 3 % of chrome alum added with continuous agitation for 1 hour, and the powder washed according to the official method. The two methods show very close agreement.

The relative efficiency of the different methods of chroming hide powder has been recently considered by Oberfell (*J. Amer. Leather Chem. Assoc.*, 1910, **5**, 434).

The subject of the solubility of the extracts is one of great difficulty from the point of view of the analyst. Many extracts which show no insoluble residue in weak solutions do so in strong ones (as used in the tanyard) and there is great doubt as to whether on dilution these pass into solution again.

The American method of estimating insoluble matter is to make up the liquor to exactly 40* BK, and take the total solids before and after filtration by evaporation. Parker has pointed out that this method is not an ideal one. It gives no indication as to the nature of the insoluble portion. The International Commission is studying this question at the present time.

The general question has been studied in detail by J. Paessler and T. Veit (*Collegium*, 1908, **322**, 295; **323**, 308 and **324**, 322) and should be referred to by those interested in this matter. Certain improvements suggested by Zeuthen (*Collegium*, 1908, 336) are under consideration by the I. A. L. T. C. Grassler reports that in rare cases tannin extracts may be coloured with analine dyes and proposes the following method for their detection: Add 2 c.c. of sodium hydroxide (1:10) to 5 c.c. of the extract, then add 5 c.c. benzene and shake well. After standing the benzene portion is passed through a dry filter-paper. Add 1 c.c. of concentrated acetic acid to the solution, which will then extract the colour from the benzene; auramine may be looked for as the most likely dyestuff.

The Value of Non-tans and Phlobathenes.—The value of the non-tans in any extract or tan liquor is open to question. Some practical authorities estimate their value as high; on the other hand, Parker (*J. Soc. Chem. Ind.*, 1910, **29**, 313) is inclined to hold the opposite view. Variations in the nature of these non-tans may give rise to these conflicting opinions. This problem has been complicated in recent years by the manufacture of extracts at higher temperature and pressure which naturally gives increased extraction of the so-called non-tans. A more detailed investigation into the nature of the non-tans (*i.e.*, the proportion of the gallic acid in the same to the tannin present) will throw further light on this subject. Stiasny (*Collegium*, 1909, **385**, 395) has shown that a higher percentage of non-tans undoubtedly slows up the penetration of the tannin proper into the pelt and Parker has shown that in some cases their presence lowers the subsequent resistance to water penetration. If their value is of a negative order experimental tanning with pure tannic acid should give the optimum effect. Figures are not available to show whether this is so in practice.

Phlobathenes, or tannin-resins play an important part in tanning. They determine the superior water-resisting power of sole leathers. The modern call for very light coloured leathers for this use, which are produced by a subsequent treatment in which bisulphites play an important part, tends to remove these more insoluble tannins, which have been deposited within the fibre substance at much cost of time and labour to the tanner. The boot manufacturer has been severely criticised on this account; and the future should see a return to a more rational standard in which the wearing and water-resisting properties are properly appreciated, and mere colour takes its proper place in the valuation of these leathers.

Treatment with Hide Powder.

The recognised methods of treating the tannin solution with hide powder have been the "filter-bell" and the "shake" methods. The former has now been discarded officially in favour of the shake method both in America and Europe. These may differ in the results given up to 4–6% (Paessler). The filter-bell method has so often been described that under the circumstances little space will be given to it here. It consists of a siphon filter connected at the upper end

with a bottle of about 10 c.c. capacity from which the bottom has been removed. The short limb is fitted by means of a rubber cork into the neck of the bottle. This is loosely plugged with glass wool, and the bottle is lightly but firmly filled with hide powder. When filled the powder is kept in place by a piece of muslin held over the lower end with a rubber band. The glass siphon is about 30 cm. long. The packed filter is placed in a beaker, and the tannin infusion added very carefully so that the hide powder is gradually wetted by capillary action. This should occupy nearly an hour. When the beaker is filled with solution the siphon is started by suction and the solution passing over collected in a measured glass. The first 30 c.c. passing is rejected and the second 60 c.c. collected if it is free from cloudiness,

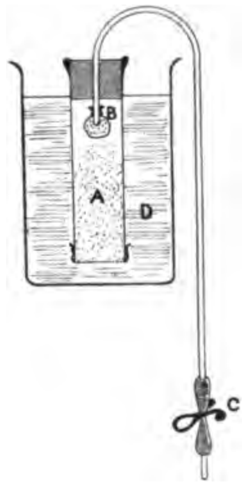


FIG. 3.

and under Procter's instructions if a little of the second portion is then allowed to drop into the first portion there should be no precipitate. This precaution is not needed with the chromed hide powder. The filtering operation should not take more than 1 hour, nor less than half an hour. This method, due to Procter, has been compared with the shake method by the International Congress, and after seven years deliberation has finally been certified as being often incorrect and misleading, since it depends on two varying factions, viz., the quality of the hide powder and the personal element of each chemist (Parker,

Collegium, 1907, **285**, 410). Figures are also given by this authority, using the then official Freiburg powder, showing the differences obtained by the two methods when using different extracts (*Collegium*, 1907, **286**, 424).

The shake method may be conducted in a so-called milk shaker as used in America (Yocum, *Leather Manufact.*, 1894, **9**), but any satisfactory method of keeping the mixture in vigorous agitation will do equally well. Bottles fixed on a frame involving not less than 60 revolutions per minute give satisfactory results.

Other Methods of Estimating Tannins.

The direct weighing of the precipitate produced by gelatin in a solution of tannin was first suggested by Sir H. Davy, who stated that the precipitate contained 40% of gallotannic acid. The method has been more recently employed by Stoddart, Macagno, Günther, Johansen, Lehmann, and others, who differ widely in their statements as to the composition of the precipitate. It undoubtedly varies greatly in composition according to the strength of the solution and other circumstances, besides which it is soluble in excess of gelatin solution and very difficult to wash free from alum or other salts employed to facilitate the precipitation. The variable nature of the precipitate, to say nothing of the difficulty of ascertaining the end of the action, is against the use of this method. Lehmann has shown that the liquid may be diluted within certain limits without notably affecting the result, while the clarification of the liquid can be effected by adding powdered glass or barium sulphate and vigorously stirring. The tannin infusion is diluted with an equal volume of saturated aqueous solution of ammonium chloride, and titrated with a 1% solution of gelatin in cold saturated ammonium chloride. The end of the action is ascertained by filtering a few drops of the liquid and testing it with a solution of gelatin on a watch-glass placed on a black surface. *Catechutannic acid* is said to give good results in this way, 1 c.c. of the gelatin reagent representing 0.139 grm. of the tannin. Johansen recommends that a little chrome-alum should be added to the ammonium chloride solution.

H. Dieudonné (*Chem. Zeit.*, 1886, **10**, 1067) ascertained the density of the infusion before and after the absorption by means of a delicate hydrometer, instead of weighing the residues obtained on evaporating

equal volumes to dryness, and gave a table of densities of solutions of gallotannic acid. The saving of time effected by ascertaining the density of the infusions, instead of evaporating them to dryness, is more than counterbalanced by the uncertainty that all tannins have the same solution-density as gallotannic acid. The suggestion is practically a revival of the obsolete process of Hammer. According to this observer, for concentrations below 5%, gallotannic acid has a solution-density of 0.004. Above that strength the increase is slightly more rapid, a 10% solution having a sp. gr. of 1.0406, and 15% of 1.0614, while a 20% solution has a sp. gr. of 1.0824. Hence each 0.1 grm. of gallotannic acid present in 100 c.c. of its aqueous solution may be regarded as increasing the sp. gr. by 0.0004.

Under ordinary circumstances, the direct observation of the increase in the weight of the hide, or other gelatinous substance employed, is impracticable, but purified catgut has been suggested by A. Girard for the estimation of the tannin and colouring matter of *wine* (*Rep. Analyt. Chem.*, 1882, **18**, 285.

W. Schmitz-Dumont (*Zeit. für öffent. Chemie.*, **3**, 209) proposed as a substitute for hide powder formalin-gelatin prepared in the following way: thick filter-paper is saturated with a 10% solution of gelatin and dried. This is then immersed for 24 hours in a 2% solution of formalin, and afterward dried at 95°. It is then cut into strips and reduced to powder by grinding, and again treated with formalin solution for 24 hours. It is then dried at 100°. In order to free the preparation from trioxymethylene it is digested in hot water until the washings give no formaldehyde reaction with alkaline resorcinol. The powder is then dried on a water-bath and is ready for use. Hide powder treated with formalin has also been tried but is unsatisfactory in its keeping qualities.

A modified method of estimating tannin by precipitation with gelatin has been described by Collin and Benoist (*Monit Scient.*, 1888, **31**, 364). They employ an aniline dye in conjunction with gelatin, and operate in presence of calcium acetate.[1] The end of the operation is indicated by the decolourisation of the liquid, the dye being precipitated with the gelatin.

A solution of tannin is made by dissolving 5 grm. of dry pure tannic acid in water, adding 0.5 c.c. of a 10% solution of mercuric iodide

[1] The use of magenta as an indicator was previously suggested by Wagner, but was found useless from the fact that it was freely absorbed by the precipitate of tannate of gelatin.

dissolved in its own weight of potassium iodide, and diluting the liquid to 1 litre. A weight of 5 grm. of gelatin is dissolved in 1 litre of hot distilled water, the liquid boiled, and sufficient white of egg added to clarify it. After cooling, 0.5 c.c. of the mercuric iodide solution is added and sufficient sodium hydroxide to render the liquid slightly alkaline. 50 grm. of pure and dry calcium acetate is dissolved in 1 litre of water, and the filtered liquid treated with a few drops of the mercuric iodide solution. This acts as a preservative of the solution.

For the assay of tannin infusions which are not coloured, a 1% solution of pure methylene blue is used. For coloured tannins or extracts either a 4% solution of Nicholson's blue BB, or a 1% solution of blue-black NBI.

For the estimation a flask is used, having a capacity of about 60 c.c. and a neck 3 cm. in diameter. 1 c.c. of gelatin solution, 2 drops of blue solution and 5 c.c. of calcium acetate are measured into the flask, which is then filled to the neck with distilled water at a temperature of 75° to 80°, by means of a burette capable of delivering 40 drops to 1 c.c.[1] A little of the standard solution of tannin is added, when the flask is closed and shaken. A precipitate is formed which rapidly rises to the surface of the liquid, and the addition of the tannin is continued drop by drop with agitation between each addition until the solution becomes colourless. The process is then repeated with a solution of the tannin-matter to be assayed, which, if acid, should previously be nearly neutralised by the cautious addition of sodium hydroxide.

The method has been tested under various conditions. Alterations in the concentration of the tannin solutions; the presence of other organic substances, such as lactates, butyrates, gallates, and gallic acids; and all the salts that accompany tannin as it occurs in commerce, have little or no influence on the results. When a large proportion of gallic acid is present, a known volume of the standard tannin solution must be added to the solution to be assayed, making the requisite correction.

Casein has been used by Nierenstein (*Chem. Zeit.*, 1911, **35**, 31) as a precipitant for tannic acid in the place of gelatin, 100 c.c. of a solution of tannin being shaken for 10 minutes with 6 grm. of casein (free from fat) and then with a further 3 grm. of the same material.

[1] The authors used specially constructed burettes. An ordinary burette with glass-tap would answer the purpose, if a special nozzle of drawn-out glass tube were attached to it by india-rubber tubing. Apparently it would not be difficult to modify the manipulation so as to employ larger quantities or more dilute solutions, and thus avoid the necessity of using a special burette.

After filtering the absorbed tannin is estimated as in the hide powder process. It is said that dextrose and gallic acid are not absorbed.

A method of assaying *tea*, originating with Allen (*Chem. News*, **29**, 169, 189), was based on the precipitation of the tannin from a hot solution by a standard solution of lead acetate, the end of the action being ascertained by filtering a few drops of the liquid and testing it with ammoniacal ferricyanide. The method was selected partly because the estimation included any gallic acid which might be present, and hence is not suited for the assay of tanning materials without some modification.[1]

R. Jackson (*Chem. News*, 1884, **50**, 179) agitated tannin infusions with lead carbonate, filtered after a few hours, and calculated the tannin from the loss of gravity, assuming a 1% solution of all kinds of tannin to be 1.0038.

Dodge (*J. Am. Leather Chem. Soc.*, 1907, **2**, 38) precipitates the tannin by means of lead carbonate, estimating the total solids and soluble solids by the official method (A. L. C. A.). Acid solutions dissolve part of the lead carbonate and this must be allowed for. Results are rather higher than with hide powder.

A. Carpené (*Gazzetta*, 1875, **5**, 120) recommends, for the estimation of the tannin in *wine*, the use of a solution of ammonio-acetate of zinc containing a large excess of ammonia, which reagent has the property of forming with the œno-tannin a tannate of zinc quite insoluble in water, in ammonia, and in excess of the reagent itself; while it gives no precipitate with alcohol, malic or tartaric acid, tartrates, glycerin, gelatin, albumin, or the iron salts of organic acids. With gallic and succinic acids, dextrose, and salts of aluminium it forms precipitates soluble in excess of the reagent and in ammonia.

On treating the wine with an excess of ammoniacal zinc acetate, a precipitate is formed, consisting of zinc tannate mixed with a small quantity of colouring matter. The wine is heated nearly to boiling to agglomerate the precipitate, which, after cooling, is filtered off and washed with a little boiling water, to remove adherent colouring matter. The precipitate is dissolved in dilute sulphuric acid, and the solution so obtained titrated with standard permanganate and indigo, as indi-

[1] M. Villon (*Bull. Soc. Chem.*, 1887, 47, 97) states that gallic acid is not precipitated by lead acetate, but this is not the case. Guyard, suggested that by using a solution of acetate of lead containing a considerable quantity of free acetic acid it might be possible to precipitate tannic acids (and colouring matter) while leaving gallic acid in solution, and then, by treating the lead precipitate with dilute sulphuric acid, a solution would be obtained in which the tannic acid could be estimated by the permanganate method. This process has been investigated and used in the Dreaper method (see page 70).

cated on page 63. The results by this method are stated to be accurate when applied to wine, but Kathreiner found that with ordinary tannin-matters the figures were very inconstant.

Figures have been given covering the use of this process with Chestnut, Mimosa, Sumac, and Quebracho, which seem to be satisfactory and agree with the official method within certain close limits (see page 31).

Ammoniacal acetate of zinc is recommended to precipitate the tannin by Lepetit (*Collegium*, 1910, 375). The excess of zinc is removed by ammonium sulphide. 20 grm. of zinc acetate are dissolved in 80 c.c. water and 12 c.c. of ammonium acetate solution added. The latter is prepared by neutralising glacial acetic acid with strong ammonia. 8 c.c. of strong ammonia are then added. To precipitate the tannin, 100 c.c. of solution containing 4.65 grm. of tannin per litre are treated with 6 c.c. of the zinc solution. After five minutes the solution is filtered through S. and S. paper 605. The zinc is removed from the clear filtrate. 4 drops of acetic acid and 1.5 of colourless ammonium sulphide being added to 65 c.c. of the filtrate. This, after-filtration, is evaporated to dryness and the residue dried at 102°–105° in a vacuum.

In Gerland's process, the tannin is precipitated by a standard solution of tartar-emetic (2.611 grm. per litre), in presence of ammonium chloride, which prevents the co-precipitation of gallic acid. The assay of *sumac* by this method is said to give results which are constantly 2/3 of those given by titration with permanganate. The tendency of the standard solution to change may be obviated by the addition of methylated spirit to the solution. Some tannins (*e. g.*, those of catechin and horse-chestnut) are not precipitated by tartar-emetic.

Richards and Palmer (Silliman's *Amer. Jour. Science*, [3], **16**, 196, 361) substituted acetate for the chloride of ammonium in Gerland's process, and ascertained the point of complete precipitation of the tannin by testing a drop of the clear supernatant liquid on a hot porcelain plate with solution of sodium thiosulphate, which produced an orange precipitate if the antimony is in excess. The standard solution of tartar-emetic contains 6.730 grm. of the dried salt per litre; 1 c.c. of this solution is equivalent to 0.01 grm. of tannin.

The Parker-Payne method of analysis (*J. Soc. Chem. Ind.*, 1904, **23**, 648) is based on the estimation of the acidity of the solution before and

after the removal of the tannins as calcium salts. 300 c.c. of N/5 solution of calcium hydroxide is added to 200 c.c. of the tannin solution of about the strength used in the official methods, and allowed to stand for 4 hours with occasional shaking. 100 c.c. are filtered and titrated with acid using phenolphthalein as an indicator. The amount of calcium hydroxide used is called the "*total absorption value.*" The tannin is then removed by precipitation with "collin," an indefinite form of hydrolised gelatin, which is very sensitive as a precipitant. The lime absorption in this filtrate is then taken and gives the "*acid absorption,*" the difference between these figures being the true tannin. It has been pointed out (Dreaper, *Chem. News*, 1904, **90**, 111, and Wood, *J. Soc. Chem. Ind.*, 1904, **23**, 1071) that this precipitation is not a satisfactory one. Procter and Bennett (*J. Soc. Chem. Ind.*, 1906, **25**, 251) also consider it unsatisfactory. Boegh (*Collegium*, 1904, **125**, 301) also shows that while the process seems to give results which compare with the hide-powder process in the case of the pyrogallol tannins, this is not so with the catechol group.

A. Casali (*Chem. Zeit.*, 1884, **8**, 98) estimated tannin by precipitation with a solution of nickel ammonium-sulphate. A volume of solution (1 c.c.) which will precipitate 0.01 grm. of gall-tannin is stated to be equivalent to 0.01497 of oak-bark tannin.

F. Becker described a method of estimating tannin by precipitation with a solution containing 5 grm. of methyl-violet per litre (*Chem. Zeit.*, 1885, **9**, 46). 50 c.c. of this solution is diluted with 450 c.c. of water at 50°, and a 1% solution of pure gallotannic acid run slowly in, with continual stirring, until the colouring matter is completely precipitated, a point readily ascertained by filtering a small sample. A similar experiment is then made with an infusion of the tanning material to be tested. The process is said to be well adapted for the assay of *sumac*, and might be found useful in most cases where the tannin is intended to be employed in dyeing or lake formation.

Ostermeyer, improving on a suggestion of Wagner, proposed to estimate tannin by a standard solution of cinchonine coloured with magenta, the end of the action being indicated by the pink tint acquired by the solution (*Chem. News*, **40**, 181). Gallic acid is not precipitated by cinchonine. Some observers have reported unfavorably of this process, and state that in certain cases the liquid acquires a red tinge long before the tannin is precipitated. The alkaloid solution contained 4.523 grm. of cinchonine sulphate, with 0.5 grm. sul-

phuric acid and 0.1 grm. fuchsin in 1 litre; each c.c. of this solution is said to precipitate 0.01 grm. of tannic acid.

Such a method for the analysis of tannin in hops and tea has been recently reviewed by Chapman, and Tatlock and Thompson, respectively (*Analyst*, 1908, **33**, 95, and *ibid*, 1910, **35**, 103). In both cases, as suggested, the tannin is precipitated from aqueous solution by quinine sulphate. The following particulars are given in the case of tea analysis: 1 grm. of tea is boiled in 400 c.c. water under a reflux condenser for 1 hour. After filtering and bringing the temperature to 15.5° add 1 grm. of ordinary basic quinine sulphate dissolved in a mixture of 25 c.c. water and 2.5 c.c. N sulphuric acid. After 15 minutes the precipitated quinine tannate is collected on a tared filter-paper, washing any precipitate remaining in the beaker into the filter with some of the filtrate, but not with water. After thorough draining, the precipitate is transferred to a weighed basin and dried at 100°. The weight is multiplied by 0.75 to obtain the tannin. This process is claimed to exclude the estimation of colouring matters as tannin. The following figures are given:

	Tannin %	
	Variations	Average
Indian teas	13.32 to 14.98	14.33
Ceylon teas	10.31 to 13.91	12.29
China teas	7.27 to 10.94	9.50

Chapman prefers cinchonine as a precipitant, and objects to extraction of hop and also tea tannins under the conditions stated. His original process is as follows: 10 grm. of hops are placed in a flask marked at 508 c.c., 400 c.c. of boiling water are added and the flask kept at that temperature for 2 hours. 50 c.c. of this filtered solution is evaporated to 15 c.c. and when cool 50 c.c. of a saturated solution of cinchonine sulphate added. After standing 2 hours the precipitate is collected on asbestos in a Gooch crucible, washed several times with a half-saturated cinchonine sulphate solution and dried at 100°, the Gooch crucible being treated with a little of the washing solution and dried as a preliminary operation. It is evident that air should be

excluded as far as possible, both in the digesting and evaporating processes or the results obtained may be low.

F. Jean (*Bull. Soc. Chem.*, 1885, **183**) has described a process of estimating tannin, based on the volume of the infusion requisite to render a solution of an iron salt opaque. The operation is conducted in a beaker 8.5 cm. in diam., placed in a good light on a black cloth, having on it a small circle of white paper about 5 cm. in diam. 5 c.c. of a solution of iron, containing 14 grm. of ferric chloride and 10 c.c. of hydrochloric acid per litre, is run into the beaker and 200 c.c. of water added. A 0.1% solution of tannin is then dropped in with constant stirring. The titration is finished when the disc of white paper is wholly invisible after the liquid has come to rest, which in the case of pure gallotannic acid occurs when 11.6 c.c. of the solution has been added. In comparing tanning materials with this it is simply necessary to take care that the infusions are approximately of the same richness in tannin, and this may be attained by extracting 1.5 grm. of European bark, 1.0 of African bark, 0.5 of quebracho, 0.5 of sumac, or 0.25 grm. of catheu, and diluting the liquid to 100 c.c. The estimation can be made very rapidly, and is said to be accurate to 0.5%. By subsequently repeating the experiment with a solution which has been treated with hide powder the error caused by gallic acid may be eliminated. This process might be useful in the dyer's laboratory for special work.

E. Durien proposed to estimate tannin by adding acetic acid and ferric chloride to the infusion, and then dropping in a standard solution of bleaching powder (5 grm. per litre) till the colour of the liquid changes suddenly to a rose-brown tint. Sugar was found not to affect the result, but gallic acid was not considered.

Musset (*Zeit. f. Anal. Chem.*, 1884, **23**, 584) described a method of titrating tannin by oxidation with iodine. 100 c.c. of a 1% solution of bark is treated with 20 c.c. of N/10 solution of iodine (12.7 grm. per litre), the flask filled to the neck with warm air-free water, and carefully closed. After 12 hours, the free iodine is reduced by standard thiosulphate solution, which should be added somewhat in excess, and the liquid titrated back with N/10 iodine and starch. By operating in a similar manner on a solution which has been treated with hide powder, the error due to the presence of gallic acid and other "not tannin" matters is ascertained,

A. Moullade (*J. Pharm. Chim.*, 1890, **22**, 153) describes a method of determining tannin by means of iodine in the presence of sodium

hydrogen carbonate. Carbon disulphide is used as an indicator. The iodine solution should contain 5.2 grm. of iodine and 7.6 grm. of potassium iodide per litre; the sodium bicarbonate solution is 1 : 10. To 10 c.c. of a tannin solution 30 c.c. of the bicarbonate solution are added, together with 2–3 c.c. of carbon disulphide. The iodine solution is introduced from a burette until a blue colour appears. Several titrations are necessary to ensure good results. In the presence of substances similar to tannin, two experiments are necessary, in one of which the tannic acid is precipitated by the gelatin; the difference between the 2 titrations corresponds to the tannin present.

According to Boudet (*J. Soc. Chem. Ind.*, 1902, **25**, 956), standard iodine solution is used in excess before and after detannising with hide powder, the excess of iodine being estimated with thiosulphate.

Gardner and Hodgson suggest a modified iodine method (*Chem. Soc. Proc.*, 1908, **24**, 273), standard iodine solution being added in excess. Sodium hydroxide solution is added drop by drop until the colour disappears, concentrated hydrochloric acid is then added to precipitate the unabsorbed iodine, which is estimated by thiosulphate solution. Gelatin is recommended to separate the tannin. (See also Proc. VII. Intl. Congress Appl. Chem., 1909, Section I.)

The detection of gallic acid in the presence of tannins is said to be achieved by titrating with iodine in the presence of sulphuric acid as well as in its absence. Sulphuric acid is said by Grassler (*Collegium*, 1910, 406) to prevent the combination of iodine with gallic acid under these conditions.

Guenez (*Compt. rend.*, 1890, **110**, 532) gives the following volumetric method for the estimation of tannin. A standard solution is prepared containing 12 grm. of tartar-emetic and 1 grm. of Poirier's green 4JE to 1 litre of water. The solution of tannin is run from a burette into 20 c.c. of the boiling coloured solution until it is completely decolourised. The standard solution may be standardized by a solution of pure oak-gall tannin of known strength. Gallic acid does not interfere with the process.

L. Roos (*J. Pharm. Chim.*, 1890, **22**, 59) gives a volumetric method adapted to the estimation of tannin in wines. A 10% solution of tartaric acid is used, made slightly alkaline with ammonia; neutral lead acetate is then added until the precipitate no longer dissolves, when the solution is filtered. Tannin is said to be completely precipitated by this solution, sodium sulphide being used as an indicator. About

25 c.c. of the wine are taken for analysis and made slightly alkaline with ammonia.

P. Wilhelm (*Rev. gén. des. mat. col.*, 1898, **11**, 307) described a method of estimating tannin by adding the tannin solution to a known volume of standardised methylene blue solution (containing a small quantity of ammonia to neutralise the free mineral acid set free) until the action is complete. The methylene blue solution should contain 12.5 grm. dissolved in 1 litre of water, and the colouring matter should be free from zinc. The tannin solution is titrated into the methylene blue solution to which a little ammonia has been added. The end-point is ascertained by spotting from time to time on stout filter-paper. When all the blue has been precipitated, the back of the spotted filter-paper remains colourless. The process has, it is claimed, given results within 2%.

L. Vignon (*Compt. rend.*, 1898, **127**, 369) described a method for the estimation of tannin by the use of silk. He claimed that silk free from silk gum absorbs tannin readily and completely from solutions of tannin materials, but does not absorb gallic acid, dextrose, etc. The tannin may be estimated either by the increase in the weight of the silk, or by the difference in the proportion of solid matters in the solution before and after treatment with silk, or by titration with permanganate. The accuracy of this method, however, depends on the nature of the tannin material employed, as silk does not appear to absorb all tannin materials in the same proportion. It also absorbs gallic acid very readily under certain conditions.

S. T. Hinsdale (*Chem. News*, 1890, **62**, 19) gave the following colourimetric method for estimating tannin in bark. The following solutions are prepared: Dissolve 0.04 grm. potassium ferricyanide in 500 c.c. water, and add to it 1.5c.c. liquid ferric chloride; this is called the iron mixture. Dissolve 0.04 grm. "pure tannin" (gallo-tannic acid), which has been dried at 100°, in 500 c.c. water; call this the tannin solûtion. 0.8 grm. of the bark is exhausted with boiling water, and the extract made up to 500 c.c. with cold water. Place six 2-ounce beakers on a white surface, and in one of them place 5 drops of the bark infusion, and in the others put 4, 5, 6, 7 and 8 drops of the tannin solution. Add to each 5 c.c. of the iron mixture, and then make a further addition of 20 c.c. of water to each after about 1 minute, and within 3 minutes observe the shades of colour. Then the number of drops of tannin solution used in the beaker which cor-

responds in shade of colour to the beaker containing the bark infusion indicates the percentage of tannin in the bark. The results are necessarily in terms of commercial gallo-tannic acid, and not in those of pure tannin or of the particular tannin in the material assayed. For substances containing over 10% of tannin, the infusion should be proportionately diluted.

Wislicenus (*Collegium*, 1904, **115**, 204) has suggested the substitution of fibroid alumina in the place of hide powder. It is said to give results which are of special value, although it is doubtful whether it will ever replace the latter in the official method, for the non-tannins are precipitated to a certain degree as well as the tannins, and possibly to a different degree from those attracted by hide powder. The alumina may be repeatedly used after ignition. It can be obtained in commerce.

Baum (*Collegium*, 1906, **230**, 373) detannises the solution in an aluminum vessel through which solution a low voltage current flows, the aluminium tannate is formed and weighed directly.

The estimation of tannin by electrolytic methods has also been suggested by Metzges (*Collegium*, 1908, **318**, 259). 250 c.c. of the solution is submitted to a current of "longue" phase and 110 volts using aluminium anodes. After 30 minutes the tannins were entirely precipitated, and the non-tannins were estimated in 50 c.c. of the solution by evaporation. Corridi, however, claims that matter other than tannins is precipitated at the same time (*Collegium*, 1909, **14**, 281). Actual results obtained with mimosa, valonia, mirabolans and quebracho are given. When analysing alkaline tannin solution anti-incrustators the solution must be acidified with acetic acid before analysis (Kopecky, *J. Am. Leather Chem.*, 1904, **2**, 45).

Determination of Colour in Extracts.—It is noticed in practice that a brightly coloured extract produces a light coloured bath and a good tannage. The colour can be tested by the optical or empirical method. In the first case, Lovibond's tintometer can be used and a permanent record of the shade can be kept. This method is satisfactory for the testing of extracts during manufacture, but is not so valuable when the resulting shade obtained on leather is the consideration. The second method of testing has been recently improved by Eitner (*Gerber* 1910, **36**, 321) where an "animalised fabric" is substituted for a piece of pelt which under old conditions was tanned under known conditions.

The animalised cotton is prepared in the following manner. A cotton material felted on one side and 1 mm. thick and 11 cm. broad is, after washing in boiling water, pressed and put on reels. This is then run through a 0.25% solution of formaldehyde and then through a 6% solution of gelatin, and subsequently dried in a protected position.

The extract to be tested is made up to 6° Bé., and 5 grm. of the animalised fabric are placed in it for a few minutes, and then churned for 12 hours. After washing in water for 10 minutes and being squeezed, it is dried very slowly at a temperature not exceeding 30°. This process is said to give uniform results and to give a good indication of the value of the extract so far as colour is concerned. It is possible that raw or gum silk would give similar results when substituted for the animalised fabric. The writer has used it for this purpose when the colour of the extract is to be tested for dyeing purposes.

Procter (*J. Soc. Chem. Ind.*, 1910, **29**, 663) suggests a variation in the method of colour measurement, and discusses the Schmidt and Haensch and the Laurient and Dubosc types of tintometer.

In testing the colour of extracts by the Lovibond method it seems that the temperature of dissolving has a great influence on the result obtained. Lamb (*Collegium*, 1910, 29) suggests that this error should be reduced by always dissolving at a temperature of 60°.

English chemists have recently adopted a colour measurement in addition to that of the ordinary tintometer figures. The standard colour represents a proportion of red to yellow (with a necessary small correction of blue). The standard strength is the quantity of extract or tannin) per 1000 parts of solution necessary to give the standard colour in a cell of 1 cm. thickness.

Examination of Tan-liquors. (See page 78).

Besides estimating the tannin and oxidisable substances in tan-liquors, it is desirable to obtain further information as to the proportion and nature of the free acids present. The acid is usually acetic, though butyric, lactic, and other acids produced by fermentation are frequently present. By titrating the liquor with lime-water, using methyl-orange as an indicator, the proportion of strong acids capable of producing "plumping," or swelling of the leather, will be roughly ascertained. Sulphuric acid is, it is said, sometimes added for this purpose.

Hoppenstedt (*J. Am. Leather Chem. Soc.*, 1906, **1**, 192) estimates free acid in tan-liquors by precipitating the tannin with quinine. 200 c.c. of diluted liquor is taken and 20 c.c. of a solution of 15 grm. of pure quinine in 110 c.c. 95% alcohol. After mixing thoroughly and filtering 100 c.c. is titrated with N/10 sodium hydroxide using phenolphthalein as indicator, as the soluble salts formed by quinine and free acids react acid to this indicator. Results are calculated as free acetic acid.

This matter has been studied in detail by Bennett and Wilkinson (*Collegium*, 1907, **289**, 441) and the conclusion come to is that no process at present known will give absolute results. The Procter lime-water method seems to give results which are useful in practice. 10 c.c. of the filtered solution to be tested is titrated with a saturated solution of lime water until a permanent turbidity is obtained due to the formation of an insoluble calcium tannate, when the free acid is neutralised. This is the only method which does not involve the removal of the tannin from the solution. In case the special tannic acid present does not give an insoluble calcium salt it is better to add a little pure tannic acid to the solution. The lime water is standardised against N/10 hydrochloric acid solution, but Procter expresses the results in terms of acetic acid. The presence of boric acid and gallic acid interfere with the value of the results obtained, so that in practice the only use that the process can claim is in estimating the acids present which will give soluble calcium salts in terms of CaO. This is of value in practice, for the part played by the acids present is to form soluble salts with the alkali of the limed hide.

The quinine method of Hoppenstedt is not favourably reported on for this purpose by these investigators. The gelatin method of Koch in which the tannin is removed by means of salted gelatin, is of little value as such coagula carry down other acids with avidity.

Bennett and Walker suggest a method in which lead oxide (3 grm.) is digested with 100 c.c. of the acid-tan liquor. All the tannins and the gallic acid and similar substances are precipitated, as well as sulphuric, boric, oxalic or carbonic acids present, so that only such acids as acetic, formic, and lactic acids are left in the solution; after filtering, 20 c.c. are titrated with N/10 potassium ferrocyanide in the presence of excess of acetic acid, using uranium acetate as an outside indicator which gives a brown colouration. Another 20 c.c. is taken, and an amount of N/10 sulphuric acid equal to that required in the

above titration added. A quantity of sodium sulphate is then added and the mixture warmed. The organic acids are thus liberated, and are estimated by N/10 potassium hydroxide using phenolphthalein as an indicator.

Grasser (*Collegium*, 1910, **406**) suggests an apparatus for estimating the acid present in tannin liquors. The carbon dioxide present is first removed by passing a current of air (free from that gas) through the liquor, absorbing in potassium hydroxide and weighing. Acetic and other volatile acids are then boiled off and titrated with N/10 alkali. The residual acids (lactic acid, etc.) of a non-volatile nature are titrated with baryta and penolphthalein after detannisation with gelatin solution (Koch's method). It must, however, be remembered that the gelatin coagulum will carry down with it free acid.

Quite recently Procter and Seymour-Jones (*Collegium*, 1910, **299**) throw doubt upon all the present methods of estimation, and fall back on the direct titration of the liquor by N/10 sodium hydroxide. They rightly point out that detannisation by gelatin or hide powder removes other acids as well. The indicator used is fluorescein. This indicator fluoresces in alkaline solution, and this property is used to indicate the end-point. The indicator only comes into play with a hydrion concentration of 10^{-6}, and consequently it only estimates the acids which actually plump the skins.

Gum arabic has been suggested as a precipitant for both gallic acid and tannic acid from tannin liquors when the acidity is to be estimated, but the process has not been accepted as a better one than the gelatin separation.

Kohnstein and Simand (*Dingl. Polyt. J.*, 1885, **38**, 256) estimated the *volatile organic acids*[1] (acetic, butyric, etc.), as follows 100 c.c. of the liquor is distilled to 30 c.c., the residue made up with water to the original bulk and again distilled, and the process repeated till the

[1] F. Andreasch (*Der Gerber*, **23**, 111) in a study of the fermentation phenomena in tan liquors, showed that the acidity of the liquor is due to the following causes:

1. Putrefactive bacteria from the hides, bates, etc., accommodate themselves to the acid reaction of tan liquors; they dissolve certain nitrogenous constituents of the hide, and thereby furnish the chief nutriment for the more specific acid-producing bacteria. In liquors which are in use, the production of acid is proportional to the hide substance present, provided sufficient quantity of carbohydrates are present.

2. Acetic acid, which in fresh tan liquors is the chief acid, is always formed by two separate processes: (1) the production of alcohol by yeasts from the sugars of the non-tannins and (2) the fermentation of the alcohol by acetic bacteria. In tan liquors it is never formed directly from carbohydrates.

3. Lactic acid is produced by several species of bacteria both from the sugars and other carbohydrates of tan liquors, and from the sugars alone by a yeast. A good supply of nitrogenous nutriment is necessary for its production, the greater part of which is furnished by the hides.

4. Butyric acid occurs only in satisfactory tan liquors.

total distillate measures 300 c.c., when it is titrated with standard alkali hydroxide and phenolphthalein, and the acidity expressed in terms of acetic acid. By adding sulphuric acid and water to the contents of the retort, again distilling and titrating the distillate, the combined acetic acid may be determined.

Another portion of the liquid (80 or 100 c.c.) is shaken with 3 to 4 grm. of freshly ignited magnesia, quite free from carbonates and calcium. The mixture is left for some hours with frequent agitation, when the brown or dirty green colour will have disappeared, and the filtered liquid will be nearly colourless, neutral, and free from tannin. The magnesia in solution is estimated in an aliquot part of the filtered solution, and will be equivalent to the total free acids of the liquor, exclusive of the tannic acid, which is completely precipitated together with the colouring matter. Another portion of the filtrate is evaporated to dryness, and the residue *gently* ignited. The ash is moistened with carbonic acid water and dried. It is then boiled with distilled water, and the solution filtered. The magnesia remaining insoluble corresponds with that which existed in the solution as magnesium salts of *organic acids*, and may be estimated gravimetrically as pyrophosphate, or dissolved in standard acid and titrated with alkali and methyl-orange or litmus. By dividing the percentage of acetic acid previously found by 3 and subtracting this figure from the percentage of MgO, the weight of the latter corresponding to the *non-volatile organic acids* of the liquor will be found; and 4.5 times this amount will be their equivalent of lactic acid. The magnesia contained in the aqueous solution of the ash is equivalent to the free *sulphuric acid* originally present.

The liquors of a set of seven handlers, in a Continental upper-leather tannery in which larch-bark was used, showed, by the above process, in grm. per 100 c.c.: Total acids reckoned as acetic, from 0.20 to 0.68; volatile acids, 0.05 to 0.46; and fixed organic acids reckoned as lactic acid, 0.05 to 0.59.

The hide-powder process for the gravimetric estimation of tannin is not applicable to the testing of acid liquors, because the hide absorbs a certain proportion of the acid which is estimated as tannin.

J. Pässler removed the greater portion of the volatile acid by repeated evaporations; the hide-powder process can then usually be applied to the testing of tan-liquors containing acetic and lactic, and similar acids, without serious error; the results are sufficiently accurate for due con-

trol of the tannin process, and said to be more accurate than those obtained by the Löwenthal or Mürkatz processes. Such evaporation must clearly be conducted *in vacuo*.

Bacterial action produces considerable changes in the composition of tannin liquors and a list of the chief of these will be found in an article by Wood (*J. Soc. Chem. Ind.*, 1910, **29**, 671).

Tannin Substitutes.

Recently sulphite cellulose liquors have come into commerce as tannin substitutes (pinewood extracts). Although these react with the hide-powder process, and may even show a result equivalent to 25% tannin, they propably do not contain any tannic acid. The permanganate process will only show 4% tannin under these conditions and is therefore preferable when this extract is suspected. If to 5 c.c. of the solution usually analysed 0.5 c.c. of aniline be added and after shaking 2 c.c. of concentrated hydrochloric acid be added, a precipitate will indicate the presence of this substitute, if it forms within 2–3 minutes.

Estimation of Sugar-content of Tanning Materials.

For a solid tanning material, a weighed quantity of the ground substance is extracted with water (1 litre at 100°). 600 c.c. of the filtered extract are concentrated to 200 c.c., and the tannins, etc., are precipitated from this solution by the addition of 20 c.c. of lead acetate solution; after 15 minutes, during which time the flask has been frequently shaken, the liquid is filtered through a dry filter, and to 100 c.c. of the filtrate 10 c.c. of sodium sulphate solution (equivalent to the lead acetate solution) are added; the lead sulphate is removed by filtration through a dried filter and 25 c.c. of the filtrate are taken for the estimation of the sugar. There are mixed in a beaker, 30 c.c. of copper sulphate solution, 30 c.c. of alkaline Rochelle salt solution and 60 c.c. of water. The whole is heated to boiling and the 25 c.c. of extract are added; the beaker is then placed in a boiling water-bath for 30 minutes. The cuprous oxide is filtered, dried, heated, and reduced in the usual manner. Should the tanning material be poor in sugar, or in case the method is applied to the analysis of a leather, which is not weighted with sugar, a larger volume than 25 c.c. may be taken for the estimation,

but a correspondingly smaller volume of water must be added to the Fehling's solution, in order that the total volume from which the cuprous oxide is to be precipitated may not exceed 145 c.c.

The quantity of material extracted must vary with its nature, as follows:

	Grm.
Oak-wood, chestnut-wood, and spent bark	30
Oak-bark, willow-bark, pine-bark, fir-bark, larch-bark, etc	20
Quebracho-wood, sumac, rove, cayota-bark, garouille, canaigre	10
Myrabolans, valonia, knoppern	7–10
Mimosa-bark	5–10
Divi-divi, algarobilla, trillo	55

In the examination of extracts, 8–20 grm. of the sample are dissolved in 250 c.c. of this solution, and without filtration, are treated with lead acetate, etc., exactly as described above, the sugar estimation being made with 25 c.c., or more, of the final filtrate under the conditions already given. Tanning liquors must generally be concentrated before precipitating with lead acetate.

In estimating the sugar in a leather it is usual to employ the 20 grm. of the finely-divided sample which have already served for the estimation of moisture, and have been extracted with carbon disulphide for the estimation of the fat. This portion is extracted in a Koch's apparatus at the ordinary temperature in the manner described above. The litre of extract is concentrated to 500 c.c., and 200 c.c. of this solution serve for the precipitation with lead acetate, etc. Some 40 c.c. of the final filtrate are used for the sugar determination.

The lead acetate solution for this work is prepared by mixing 300 grm. of lead acetate with 100 grm. of litharge and 50 c.c. of water, heating on the water-bath, with replacement of evaporated water, until the mixture is white in colour, digesting with a litre of cold water, and filtering.

An inspection of the table (page 102) will show that those materials which contain a high ratio of sugar to tannin are the ones which have always been used for the tanning of such leather as requires an acid liquor for the production of full weight. It must not be forgotten, however, that although there is evidence that sugars give rise to acid by fermentation they may not be the sole cause of acidity in the bath.

	Mean tannin-content	"Sugar"-content			Proportion of acid-yielding substances to 100 tannin
		Mean	Minimum	Maximum	
	%	%	%	%	
Pink-bark extract	25.00	7.84	4.58	9.44	31.4
Pine-bark	11.63	3.53	2.65	4.47	30.4
Oak-bark (young)	10.10	2.65	1.75	3.46	26.2
Divi-divi	41.50	8.39	7.98	8.83	20.2
Willow-bark	10.00	2.16	....	....	21.60
Canaigre	30.00	6.24	....	....	20.80
Algarobilla	43.00	8.23	6.24	10.49	19.1
Myrabolans	30.00	5.35	3.15	7.05	17.8
Sumac (Italian)	28.00	4.53	....	....	16.2
Oak-bark extract (Slavonic).	28.00	3.07	2.47	3.92	11.0
Chestnut-wood extract (normal liquid).	30.00	2.87	2.61	3.53	9.6
Valonia	28.80	2.69	1.21	3.57	9.3
Cayota-bark	22.00	1.65	....	....	7.5
Hemlock-bark	12.32	0.71	....	....	5.76
Trillo from Valonia	43.50	2.41	....	....	5.5
Garouille	25.00	1.00	0.67	1.51	4.0
Gambier	47.18	1.85	....	....	3.92
Rove	29.00	1.13	....	....	3.9
Quebracho extract (solid).	70.00	2.41	1.04	3.80	3.4
Mimosa-bark	32.00	0.91	0.33	1.57	2.8
Knoppern	30.00	0.65	0.54	0.71	2.2
Catechu	39.89	0.50	....	....	1.25
Quebracho-wood	22.00	0.25	0.10	0.65	1.1

Detection of Adulteration in Sumac and Other Extracts.

Sumac (*Rhus coriaria*) tanned book-binding leathers are less likely to be affected by light, gas fumes, or to decay or "rot," so that adulteration is here particularly detrimental. This satisfactory condition is probably due to the absence of catechol tannins in the pure article. Many species of the *Rhus* family are used to adulterate sumac, but *Pistacia lentiscus* is chiefly used. Procter's bromine water test or a microscopical examination is the best way of detecting these leaves and twigs. Nierenstein and Webster (*Collegium*, 1907, **265**, 244) suggest the use of the diazobenzene chloride test. 5 grm. of the sumac are heated for about 6 hours and filtered. 10 c.c. of the extract are placed in narrow beakers and 10 c.c. of 2% solution of diazobenzene chloride added and the mixture allowed to stand 12 hours with as little exposure to air as possible. The precipitate is filtered and washed with dilute hydrochloric acid, then with distilled water, and the nitrogen estimated by Kjeldahl's method.

Sumac is also adulterated with leaves of *Tamarix africana*. In order to detect these adulterations the use of the following property of a pure sumac decoction has been suggested: If lead acetate in po-

tassium hydroxide is added to a decoction of sumac and the mixture concentrated, a brownish-red liquid is obtained, which assumes a claret colour when diluted with water. The intensity of this colour will depend on the amount of sumac present, and since the decoctions of the leaves used for adulteration do not give this colour, the reaction may be employed not only for their detection, but also for their quantitative estimation by colorimetry (Spica, *Gazetta*, 1897, **27**, 349).

For this purpose 5 grm. of the sample are boiled for half an hour in 500 c.c. of water. After cooling, the liquid is made up to its original volume and filtered. 25 c.c. of the filtrate are run into a flask together with 5 c.c. basic lead acetate (sp. gr. 1.184, containing 250 grm. basic lead acetate per 1000 c.c.) and 15 c.c. potassium hydroxide solution (sp. gr. 1.155). The mixture is shaken and then boiled until the volume has decreased to 15 c.c. In the case of pure sumac, the concentrated reddish-brown liquid is almost perfectly clear. The presence of an insoluble precipitate is sufficient to indicate the probability of adulteration. To obtain the amount of adulteration the liquid is diluted to 250 c.c., filtered and examined colorimetrically. The intensity of colour of pure sumac is equal to that of a solution of 0.15 grm. of safranin in 1000 c.c. water, which may be taken as a standard in case a pure sumac sample is unavailable. A suitable colorimeter may be employed for the determination.

Spica also furnishes the following method of determining the presence of *Pistacia lentiscus* in sumac: 0.5 grm. of the sample is boiled in a test-tube with 5 c.c. of an 18% solution of potassium hydroxide. Pure sumac gives a brownish-yellow colour becoming paler when diluted with water. If *lentiscus* is present the solution assumes a brown colour with a violet tint and on dilution this changes to a chestnut brown.

As the ash of *Tamarix africana* contains sulphates, their presence may be detected in the following manner: 1 grm. of the sample is boiled for half an hour with 100 c.c. of water; the filtered liquid is acidified with nitric acid, and barium chloride is added. It is said that if *Tamarix* is present the solution will become turbid.

F. Andreasch (*Gerber*, 1898, **24**, 573) gave the following method for the analysis of sumac containing adulterants from 8 to 60%: About 20 grm. of material is treated with a litre of water at 60° and filtered. The addition of several drops of formaldehyde (40% solution) gives a light yellow flocculent precipitate if *Pistacia* is present;

care must be taken to have the solution neutral. Arsenious acid solution, when warmed with a solution of *Pistacia*, gives a white precipitate; mercurous nitrate gives a yellow precipitate, which gradually turns green. A pure sumac should give no precipitate with formaldehyde. Sulphurous acid and potassium cyanide give no indication with pure sumac; if *Tamarix* is present, however, sulphurous acid produces a white precipitate or cloudiness; and potassium cyanide gives a dirty yellow precipitate. Sicilian sumac should never have less than about 22% of tannin, and not more than 18% of non-tannins. As the tannin in *Pistacia* and *Tamarix* is said to range from 8 to 17% and the non-tannins from 20 to 26%, a sample of commercial sumac should not contain less than 20% of tannin and more than 20% of non-tannins.

Myrabolans are used in blending extracts, although not so cheap a source as mangrove. Their presence can be detected by the Stiasny test (see page 8).

Dietrich (*Ber. Pharm. Ges.*, 1897, **7**, 153), states that an alcoholic solution of gambier (*Nauclea Uncaria, Gambier*), when rendered strongly alka-line with sodium hydroxide gives a strong green fluorescence to petroleum ether when shaken with it.

The bark of chestnut-oak (*Q. prisnus*) exhibits a strongly blue fluorescence in alkaline solution. This is best seen after precipitating the tannin present with ammoniacal zinc solution.

The adulteration of tannin extracts is, according to Eitner (*Gerber*, 1907, **61**, 700), chiefly confined to quebracho and mimosa. Chestnut-oak and hemlock are not often adulterated. Mangrove is used to adulterate quebracho. The former also sometimes is adulterated with grape-sugar. Mangrove is an inferior tannin material and may give trouble in the yard. Divi-divi and valonia extracts have been found to be adulterated.

ANALYSIS OF LEATHER.

By W. P. DREAPER, F. I. C.

The study of the processes involved in tanning have been undertaken by many investigators. The many text-books on the subject should be consulted as well as articles by Herzog and Rosenburg (*Jeit. Chem. Ind. Kolloide*, 1910, **7**, 222), Procter (*J. Soc. Chem. Ind.*, 1910, **29**, 329), Gordon Parker (*J. Soc. Chem. Ind.*, 1910, **29**, 912).

The scheme of analysis of leather tanned with vegetable tannins as originally suggested by von Schroeder is as follows:

1. Sp. gr. found by the displacement of mercury in a graduated measuring cylinder or by Simand's direct method (*Chem. Tech. Untersuchungmethoden*, 1893, **2**, 55). Mean of 94 samples (18% OH_2) $=1.012$.
2. Moisture by drying in the air at 105°.
3. Total ash, and ash of extract.
4. Fat, natural and added and its properties.
5. Organic extractive matter (tannin and non-tannin).
6. Sugars.
7. Nitrogen by Kjeldahl's method.
8. CaO and SO_3.

From the nitrogen in the dry ash-free leather the pure hide substance is calculated as follows:

$$H = \frac{L + NL}{Nb.}$$

H = dry ash-free hide. L = dry ash-free leather substance. NL = nitrogen in dry ash-free leather substance. Nb = nitrogen in the dry ash-free hide as prepared for tanning, the % of N being constant for any kind of hide. The difference between H and the pure leather substance gives the amount of combined tannin. The tanning number D (Durchgerbungszahl) may be expressed numerically when G = combined tannin, as:

$$D = \frac{G}{H} \times 100 = \frac{L - H}{H} \times 100 = \left(\frac{L}{H} - 1\right) 100 = \left(\frac{Nb}{NL} - 1\right) 100.$$

It being assumed that a complete tannage may be represented by dry hide substance combined with its own weight of tannin.

This method of detailed analysis, as originally devised by von Schroeder, is in use in a modified form to-day. The vegetable tanned leather is cut into thin shavings or powdered by means of a rasping machine. Under modern conditions, samples are analysed for (*a*) moisture, (*b*) mineral ash, (*c*) oil, (*d*) water-soluble matter, (*e*) the mineral ash in (*d*), (*f*) hide substance is deduced from the percentage of nitrogen present. The "pure leather" is estimated by difference:

$$100-[a+(b-e)+c+d]=\text{pure leather.}$$

From this figure the tannin substances present may be estimated by subtracting (*f*) from the result. The ratio tannin / hide substance is called the "degree of tannage" and is of practical value to the tanner in determining the quality of the leather, and also to the currier or dresser of leather. It is obvious that with such a method the question of the evenness of the tanning must be taken into consideration. This can be roughly acertained by the appearance of the section of the leather. It is found in practice that when a complete penetration is observed, and the above ratio indicates a low tannage, that this may generally be regarded as evidence of the use of some accelerating process, such as "drumming" or mechanical movement, during the tanning process, and that the tanning is correspondingly incomplete in its nature. In conjunction with the determination of such physical properties of leather as that of penetration of water, water absorption, tensile strength, etc., this ratio has come into general use for the estimation of its value.

A source of error in the calculation of results, due to the fact that part of the mineral ash is also extracted as soluble matter in different portions taken for these estimations must be allowed for by incinerating the water-extracted sample and deducting this from *b* as indicated. The mineral constituents may in this way be estimated as water soluble and insoluble respectively. Such an error may reduce the leather substance found by nearly 1% and correspondingly alter the "degree of tannage" returned by over 2%. It has also been pointed out that the actual figures obtained for insoluble ash may be lower than the ac ual insoluble mineral matter present by 0.02–0.04%, owing to certain alterations which take place on incineration (Parker and Paul, *J. Soc.*

Chem. Ind., 1910, **29**, 316), so that it may be better to estimate the leather substance by subtracting the weight of insoluble ash (with possibly an addition of 0.03% for the above correction) from that of the dry leather residue after water extraction (*d*). This error which occurred in the original method of calculation may introduce an error of 0.5% to 2.4% in the "degree of tannage" figures, and this error will be in excess at the present time owing to the much higher ash in many modern leathers due to the bisulphite treatment and use of extracts in tanning. The analyst is therefore advised to use the latter method of calculation in the place of the original method of von. Schroeder.

No particular details are necessary in explanation of the methods used in (*a*) or (*b*). In the estimation of oil (*c*) the extraction is carried out with petroleum ether. The water-soluble matter is estimated in the fat-extracted sample (*c*) by washing out with warm water (50° to 60°) by slow percolation. Parker and Paul advise the use of certain refinements which are set out in the accompanying illustration (Fig. 3).

A water-bath governed by a thermo-regulator contains a number of small glass vessels or inverted Procter filter bell extractors, plugged at the end with glass wool. The film of the water which may correspond with the flow of 1000 c.c. per 24 hours when 20 grm. of leather are used, is so arranged that it passes through a lengthened glass tube set in the water-bath itself so that the temperature of extraction is standardised. In practice the latter should never exceed 55–60°. The following figures obtained in this way are of great interest, for they indicate the differences obtained in practice between the original method of calculation marked S and the newer method marked E respectively. In Table I the results obtained with pure vegetable tanned leathers; Table II gives results obtained when using mixed tannins or extracts, and Table III deals with adulterated leathers in commercial use. In the latter case the differences are so large that this figure might be of some use in determining the nature of the tanning.

It is also stated (*J. Amer. Leather Chem. Assoc.*, 1910, **5**, 426) that an error is observed in the amount of water soluble matter when this is taken on the dried and exhausted sample at compared with that obtained when the original sample is tested.

The American Leather Chemists' Association have specified a provisional method of leather analysis of which the following is an abstract:

1. **Preparation of Sample.**—Must be reduced to as fine a state of division as possible by cutting or grinding.

2. **Moisture.**—Dry 10 grm. of leather for 16 hours at 95–100°.

3. **Fats.**—Extract 5–10 grm. of air-dry leather in a Soxhlet using petroleum ether boiling below 80°.

4. **Ash.**—Incinerate 10–15 grm. in a tared dish at a full red heat.

5. **Water-soluble Material.**—Digest 30 grm. in a percolator over night, extract with water at 50° for 3 hours. Total volume of solution to be 2 litres. Determine total solids and non-tannins by official method for extract analysis.

6. **Glucose.**—To 500 c.c. of solution obtained by extraction add 20 c.c. of normal lead acetate, shake well, stand for 1 hour and filter. To 400 c.c. of filtrate add dry sodium carbonate and filter. Add 5 c.c hydrochloric acid (conc.) and boil for 2 hours, allowing the solution to evaporate to 90 c.c. (about). Add dry sodium carbonate until solution is neutral (about), make up to 100 c.c., and filter if necessary. Take an aliquot part containing not more than 0.25 grm. of sugars, add to 60 c.c. of Allihn's Fehling's solution, dilute with water to 145 c.c., cover with watch-glass, bring to boil, and set in a boiling water-bath for 30 minutes exactly. Filter through asbestos mat in Gooch crucible, wash with hot water, and finally with alcohol, dry in water oven for 1 hour, cool and weigh. Multiply weight of CuO by 0.8883 and calculate as glucose.

Glucose may also be estimated in leather in the following manner: The water extract from the leather may be treated with calcined magnesium hydroxide to remove any tannin. The solution is then rendered alkaline with sodium hydroxide and boiled with 0.05 grm. of *o*-nitrophenylpropiolic acid. Any indigo formed is filtered off, washed with very dilute sulphuric acid, then with dilute alcohol and dissolved in chloroform. The solvent is evaporated and the indigo weighed, any inorganic matter in the ash being deducted from the weight of the same. The glucose is calculated from the weight of indigo found.

7. **Nitrogen.**—Gunning's modification of Kjeldahl's method (*A. O. A. C. Bull.*, No. 107, 1907) is used (see Vol. 1, p. 59).

Thuau and Korsak (*Collegium*, 1910, 364) propose a modified method of estimating the nitrogen in leather: 0.25 grm. of leather and 5 c.c. of concentrated sulphuric acid are gently boiled in a flask. A few centigrm. of manganese dioxide are then added and the mixture

boiled until it is colourless and clear. The resulting ammonium sulphate is estimated by decomposition by the addition of sodium hypobromite in the presence of excess of sodium hydroxide. Nitrogen is given off which is measured in a special apparatus. The analysis of leather in some of its details has also been considered by Veitsch (*J. Amer. Leather Chem. Assoc.*, 1910, **5**, 426).

As Procter has specially pointed out the analysis of the ash of the leather is useful. The presence of chromium sesquioxide, lead, sulphate, tin, are the substances most likely to be found.

The microscopical examination of the leather is important and must be considered by all who are interested in the examination of leathers from the manufacturing point of view.

The following tables due to Parker will give some idea as to the composition of leathers of to-day and at the same time indicate the differences between the (*s*) older method of calculating results and (*e*) the newer one (see pages 112 to 114). These results indicate the average differences as well, which are also instructive in their way, especially in the case of adulterated leathers, and once more indicates the absolute need of a standardised method of analysis, as in the case of the tannins.

Estimation of Free Acid.—This gives great trouble, owing to the small amount of acid usually present (Jean, *Chem. Zeit.*, 1893, 317). If the sample gives any indication of free acid, it is extracted in a Soxhlet apparatus and a little sodium carbonate is added to the extracting solution in the boiling flask. It is said to under these conditions any free sulphuric acid is extracted from the leather, leaving any sulphates behind in the leather. On distilling off the alcohol, any free sulphuric acid therefore remains as sodium sulphate and can be estimated in the usual manner. Gordon Parker points out that it is difficult to get reliable results when testing the amount of sulphuric acid in dyed leathers, owing to the presence of sulphonic acid dyes. A difficulty is also found when sulphited extracts have been used.

PHYSICAL TESTS.

The water-penetration test consists of a cylinder made of copper 14 in. high and 2 in. in diameter with a flange on the bottom with screw holes on which a second ring may be screwed with a 2-in. hole in the centre, like a large washer. A round piece of leather is now cut about 3 in.

in diameter, placed on the bottom of the cylinder and by aid of the metal washer screwed or clamped on to the bottom of the cylinder as tightly as possible. The cylinder is now filled with ordinary cold water to a height of 12 in., fastened in a retort stand, a mirror is put underneath and the time is noted that the water takes to penetrate through the leather. The leather is always clamped in grain side upward. Tests are made generally in triplicate and the mean of the 3 is taken, and it is not sufficient to observe the time that the water takes to come through in

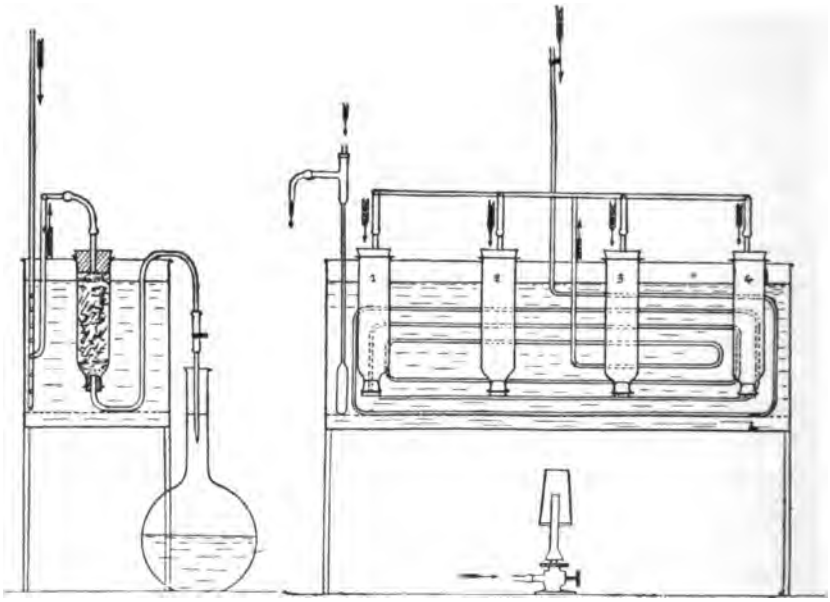


FIG. 4.

one spot as there may be a flaw in the leather; the leather on removal is cut with a knife to see that the water has penetrated right through. Good sole leather generally takes about 170 to 250 hours.

The Parker water absorption test is as follows: Several strips of the leather to be tested are cut 1 in. in width and about 6 in. long, they are then, by any suitable means (copper wire or otherwise), suspended in a beaker of water so that 1 in. of leather is in water. This may be marked with a pencil; the leather is then marked every 1/4 in. with pencil and at the end of 24 hours suspension in water, the height that the water has risen by absorption is noted. The tighter and more

compact the leather is, the less the water absorption, but a porous, poorly tanned leather may give an absorption of 2 in. or even 3 in. in 24 hours.

The above physical tests are those adopted at the Leather Sellers' Technical College, London, and are generally recognised in the trade for their efficiency and usefulness.

The penetration of water through leather may also be tested by drawing 10 c.c. of water through a piece of leather of known thickness by means of a vacuum of known magnitude. The result is stated in terms of the quantity of water percolating through 1 c.c. of leather in 1 minute (Thuau and Korsak, *Collegium*, 1910, 229).

Complete Analysis of Leathers, giving Von Schroeder's Exact Method and Calculations.

TABLE I.

TANNED LEATHERS WITHOUT EXTRACT.

Class of leather		Moisture	Ashes		Fat	Sol. matter	Pure leather subst	Total	Leather subst.		Degree of tannage T.G./H.S. %	Difference
			Total	From insol. mineral matter					Hide subst	Tannin comb.		
English sole	s	17.08	0.59	....	0.84	20.0	61.49	100.0	35.37	26.12	73.8	....
	e	17.08	....	0.29	0.84	20.0	61.77	99.98	35.37	26.40	74.6	0.8
English sole	s	16.8	0.72	....	0.92	18.4	63.16	100.0	34.9	28.26	80.9	....
	e	16.8	....	0.21	0.92	18.4	63.60	99.93	34.9	28.70	82.2	1.3
Pure hemlock, U.S.A.	s	17.06	0.74	....	0.89	17.4	63.91	100.0	38.50	25.41	66.0	....
	e	17.06	....	0.27	0.89	17.4	64.32	99.94	38.50	25.50	67.0	1.0
Venezuela sole	s	18.02	0.63	....	0.38	5.45	75.52	100.0	48.05	27.47	57.1	....
	e	18.02	....	0.11	0.38	5.45	76.07	100.03	48.05	28.02	58.3	1.2
Californian oak	s	16.72	0.81	....	1.05	16.50	64.92	100.0	33.3	31.62	94.6	....
	e	16.72	....	0.19	1.05	16.50	65.45	99.91	33.3	32.15	96.5	1.9
West of England	s	17.22	0.86	....	1.09	20.20	60.63	100.0	35.0	25.63	73.2	....
	e	17.22	....	0.12	1.09	20.20	61.32	99.95	35.0	26.32	75.2	2.0
Oak sole	s	17.31	0.46	....	0.73	19.70	61.80	100.0	36.4	25.4	69.7	....
	e	17.31	....	0.05	0.73	19.70	62.20	99.99	36.4	25.8	70.8	1.1
Oak sole	s	17.51	0.48	....	0.91	19.05	62.05	100.0	36.9	25.15	68.1	....
	e	17.51	....	0.09	0.91	19.05	62.53	100.09	36.9	25.63	69.4	1.3
French pure oak	s	18.08	0.76	....	0.11	7.28	73.77	100.0	42.6	31.17	73.1	....
	e	18.08	....	0.07	0.11	7.28	74.33	99.87	42.6	31.73	74.4	1.3
French pure oak	s	18.6	0.58	....	0.42	7.04	73.36	100.0	43.2	30.16	69.8	....
	e	18.6	....	0.04	0.42	7.04	73.82	99.92	43.2	30.62	70.9	1.1
Canadian hemlock	s	16.52	0.88	....	2.06	15.1	65.44	100.0	33.6	31.84	94.7	....
	e	16.52	....	0.13	2.06	15.1	66.30	100.11	33.6	32.7	97.3	2.6
Average	s	17.35	0.68	....	0.85	15.10	66.00	100.	37.98	28.02	73.7	....
	e	17.35	....	0.14	0.85	15.10	66.51	99.97	37.98	28.53	75.1	1.4

TABLE II. MIXED TANNAGE.

Class of leather		Moisture	Ashes: Total	Ashes: From insol. mineral matter	Fat	Sol. matter	Pure leather subst.	Total	Leather subst.: Hide subst.	Leather subst.: Tannin comb.	Degree of tannage T.G./H.S. %	Difference
English sole	s	15.6	1.02	....	0.8	16.6	65.98	100.0	35.6	30.38	85.3	....
	e	15.6	....	0.18	0.8	16.6	66.7	99.88	35.6	31.10	87.3	2.0
English sole	s	16.52	0.99	....	1.10	18.2	63.19	100.0	34.7	28.49	82.1	....
	e	16.52	....	0.23	1.10	18.2	63.90	99.95	34.7	29.2	84.1	2.0
English sole	s	16.8	0.85	....	0.9	18.85	62.6	100.0	36.1	26.50	73.4	....
	e	16.8	....	0.17	0.9	18.85	62.6	99.92	36.1	27.10	75.0	1.6
French sole	s	15.8	1.4	....	1.4	18.1	63.3	100.0	36.0	27.3	75.8	....
	e	15.8	....	0.12	1.4	18.1	64.48	99.90	36.0	28.48	79.1	3.3
French sole	s	16.45	1.62	....	1.1	17.8	63.03	100.0	35.6	27.43	77.0	....
	e	16.45	....	0.14	1.1	17.8	64.5	99.99	35.6	28.9	88.1	4.1
French sole	s	16.34	1.31	....	0.95	17.5	63.9	100.0	39.2	24.70	63.0	....
	e	16.34	....	0.12	0.95	17.5	65.0	99.91	39.2	25.80	65.8	2.8
French upper	s	16.1	1.20	....	2.8	18.7	61.20	100.0	36.8	24.4	66.3	....
	e	16.1	....	0.21	2.8	18.7	62.1	99.91	36.8	25.3	68.7	2.4
German split	s	17.02	1.18	....	0.	19.0	62.8	100.0	40.9	21.9	53.5	....
	e	17.02	....	0.18	0.	19.0	63.8	100.0	40.9	22.9	55.9	2.4
German split	s	16.0	1.45	....	0.	22.2	60.35	100.0	40.6	19.75	48.6	....
	e	16.0	....	0.25	0.	22.2	61.5	99.95	40.6	20.9	51.4	2.8
English upper	s	12.65	1.03	....	34.21	3.82	48.29	100.0	30.3	17.99	59.3	....
	e	12.65	....	0.12	34.21	3.82	49.14	99.94	30.3	18.84	62.2	2.9
Spanish sole	s	14.9	1.50	....	2.4	13.6	67.6	100.0	40.2	27.4	68.1	....
	e	14.9	....	0.17	2.4	13.6	68.8	99.87	40.2	28.6	71.1	3.0
Italian sole	s	16.0	1.7	....	1.35	19.75	61.20	100.0	37.8	23.4	61.9	....
	e	16.0	....	0.2	1.35	19.75	62.60	99.90	37.8	24.8	65.6	3.7
English sole retained	s	16.40	2.4	....	1.3	18.90	61.0	100.0	35.05	25.95	74.0	....
	e	16.40	....	0.14	1.3	18.90	63.2	99.94	35.05	28.15	80.3	6.3
American mixed	s	16.87	0.89	....	0.91	13.6	67.73	100.0	37.1	30.63	82.5	....
	e	16.87	....	0.16	0.91	13.6	68.45	99.99	37.1	31.35	84.5	2.0
South African sole	s	18.27	1.61	....	1.21	15.2	63.71	100.0	38.2	25.51	66.7	....
	e	18.27	....	0.07	1.21	15.2	65.32	99.97	38.2	27.12	70.9	4.2
English drum tanned	s	16.04	1.24	....	1.71	23.95	57.06	100.0	35.84	21.22	59.2	....
	e	16.04	....	0.18	1.71	23.95	58.12	100.00	35.84	22.28	62.1	2.9
Spanish sole	s	18.26	1.16	....	0.18	11.75	68.65	100.0	40.55	28.10	69.2	....
	e	18.26	....	0.14	0.18	11.75	69.56	99.89	40.55	29.01	71.5	2.3
English sole	s	14.12	0.94	....	0.81	22.92	61.21	100.0	37.3	23.91	64.1	....
	e	14.12	....	0.15	0.81	22.92	61.95	99.95	37.3	24.65	66.0	1.9
Average	s	16.12	1.305	....	2.95	17.24	62.37	100.0	37.10	25.27	68.1	....
	e	16.12	....	0.162	2.95	17.24	63.46	99.94	37.10	26.36	71.0	2.9

TABE III.

Adulterated Leather.

Class of leather		Moisture	Ashes		Fat	Sol. matter	Pure leather subst.	Total	Leather subst.		Degree of tannage T.G./H.S. %	Difference
			Total	From insol. mineral matter					Hide subst.	Tannin comb.		
German sole	s	17.6	2.2	....	1.60	22.3	56.30	100.0	34.4	21.9	63.6	....
	e	17.6	....	0.18	1.60	22.3	58.2	99.88	34.4	23.8	69.1	5.5
German upper	s	15.50	2.07	....	2.81	28.4	51.22	100.0	30.8	20.42	66.3	....
	e	15.50	....	0.25	2.81	28.4	53.0	99.96	30.8	22.2	72.0	5.7
Belgian sole	s	16.78	2.6	....	1.90	20.52	58.20	100.0	34.2	24.0	70.1	....
	e	16.78	....	0.19	1.90	20.52	60.5	99.89	34.2	26.3	61.8	6.7
Italian sole	s	17.1	1.91	....	1.8	21.4	57.79	100.0	35.6	22.19	62.3	....
	e	17.1	....	0.17	1.8	21.4	59.5	99.97	35.6	23.9	67.1	4.8
American sole	s	17.6	3.2	....	1.6	22.6	55.0	100.0	33.3	21.7	65.1	....
	e	17.6	....	0.28	1.6	22.6	58.0	100.08	33.3	24.7	74.1	9.0
English sole	s	17.86	4.82	....	1.37	16.90	59.05	100.0	43.3	15.75	36.3	....
	e	17.86	....	0.15	1.37	16.90	53.75	100.03	43.3	20.45	47.2	10.9
Belgian sole	s	17.9	4.95	....	1.2	23.8	52.15	100.0	33.8	18.35	54.2	....
	e	17.9	....	0.21	1.2	23.8	56.83	99.94	33.8	23.03	68.1	13.9
Average	s	17.19	3.10	....	1.75	22.27	55.67	100.0	35.06	20.61	58.7	....
	e	17.19	....	0.20	1.75	22.27	58.64	99.95	35.06	23.48	66.9	8.2

DYES AND COLOURING MATTERS.

By W. P. DREAPER, F. I. C.,

AND

E. FEILMANN, B. Sc., F. I. C. Ph. D.

Until the middle of the 19th century, nearly all the colouring matters used for dyeing were either such as existed ready-formed in the vegetable or animal kingdom, or were producible from natural products by very simple chemical processes. In a few cases, however, as when lead chromate or Prussian blue was formed as an insoluble precipitate in the fibre, the dyes were strictly of artificial origin. Now, the vast majority of the colouring matters used as dyes—as distinguished from mere paints or pigments—are products of organic synthesis, being in almost all cases obtained, by a series of highly involved processes, from coal-tar.

Picric acid and aurin are the oldest of the coal-tar colours, but the coal-tar colour industry may be said to date from 1856, when Perkin accidentally discovered the violet dye called mauve in the course of an investigation having as its object the synthesis of quinine. In 1859 Hofmann synthesised Aniline Red (magenta), and in the following year Verguin manufactured it in quantity. In 1860, rosaniline or magenta first became of commercial importance, owing to the simultaneous discovery of the arsenic-acid process by Medlock and Nicholson. Phenylated blues were first produced by Girard and DeLaire in the same year, but their insolubility rendered their application limited until Nicholson, in 1862, discovered a method of rendering them soluble by conversion into sulphonic acids. The first azo-dye, amino-azobenzene, was introduced by Simpson, Maule, and Nicholson in 1863, under the name of Aniline Yellow, and in the same year the methylated and ethylated rosanilines, known as Hofmann's Violets, were manufactured by the same firm. Aniline Black, also, was discovered by Lightfoot in 1863. Azo-diphenyl Blue, the first of the colouring matters now known as indulines, appeared in 1864, as also did dinitronaphthol or Manchester Yellow. In 1866, triamino-azobenzene

or Bismarck brown was first made, and in the same year Coupier's nitrobenzene process of manufacturing magenta was introduced. In 1868, Graebe and Liebermann announced their discovery of the constitution of alizarin, and in the following year this colouring matter was first manufactured from anthracene. Galleïn and fluoresceïn were discovered in 1871, and in 1874 tetrabromofluoresceïn was introduced as a dye by Caro, under the name of eosin. Diamino-azobenzene or chrysoïdine was introduced by Witt in 1875. Methylene Blue and Acid Magenta were introduced by Caro in 1877, and in the same year the fugitive Aniline Yellow was rendered valuable and stable by Grässler, by conversion into a sulphonic acid. In 1878, the tropæolins, Fast-Red, Naphthol-Scarlet, and other sulphonated azo-colours were first manufactured; and Malachite Green dates from the same year. In 1879, the first of the secondary azo-dyes appeared under the name of Biebrich Scarlet. The synthesis of indigo was effected by Baeyer in 1880, and indophenols were introduced by Koechlin and Witt in 1881. In 1883, Caro's process of manufacturing colouring matters of the rosaniline group by the aid of phosgene gas was patented. Congo-red, the first of the numerous class of benzidine dyes, which dye cotton without a mordant, was patented by Böttiger in 1884, and this was followed in the same year by Chrysamin. In 1885, Azo-Blue and Benzazurin appeared, and in 1886 the Benzopurpurins were patented. Numerous other dyes are constantly appearing, and in many cases they exceed in fastness, brilliancy, or cheapness those already in the market.

In 1894 Vidal patented the first sulphide dyestuffs, obtained by the action of sulphur and sodium sulphide on aromatic amino- and hydroxy-compounds, and in 1901 Bohn's discovery of the production of indanthrene, the first of a new class of vat dyestuffs, was patented.

CHEMICAL NATURE OF COLOURING MATTERS.

Salts of colour-bases or phenylated ammonia derivatives, are employed in dyeing the hydrochloride being the usual form of combination, though the acetate, nitrate, and other compounds are employed in certain cases.

In the free state, the colour-bases are usually unsoluble, colourless, or only slightly coloured. Most of them can be converted into soluble and colouring matters by treatment with strong sulphuric acid (Salts of sulphuric acids).

Many dystuffs are *salts of colour acids* which, like all acids, contain hydrogen in such a condition that it is readily replaceable by metals. It may form part of a hydroxyl group, OH, as in picric acid; of a sulphonic group, SO_3H, as in helianthin; of an imino group, NH, as in aurantia; or of a carboxyl group, COOH, as in the scarlet obtained from salicylic acid. Those colouring matters which owe their acid properties to the hydroxyl groups are very weak acids (*e. g.*, alizarin, aurin); but the acid characters are considerably intensified by the introduction of halogen or nitro-groups. Thus the eosins and nitrophenols have stronger acid characters than fluorescein and phenol from which they are derived. The free sulphonic acids are often insoluble or only sparingly soluble in water, but their alkali-metal salts are soluble. Some of the acid colouring matters unite with metallic hydroxides (*e. g.*, those of tin, iron, chromium, aluminium) to form insoluble compounds called lakes.

Of neutral dyestuffs, indigoid dyestuffs are notable examples. Possibly the very large class of sulphide dyestuffs, the constitution of which is at present doubtful comes under this heading.

RELATIONS OF COLOURING MATTERS TO FIBRES.

While the chemist defines dyestuffs and colouring matters as acid, basic, or neutral, the dyer classifies them according to their behaviour with fibres. Thus, excluding indigo, aniline black, Prussian blue, and a few other colouring matters such as the "ingrain" dyes which are produced by some chemical reaction occurring within the fibre itself, dyes may be classed as substantive or direct, and adjective or mordant.

Substantive dyes are absorbed directly from their solutions by the fibre, without requiring the intervention of a mordant. The animal fibres (*e. g.*, silk and wool) possess an affinity for most of the coal-tar colours, and in many cases under the conditions of dyeing absorb them so completely that the dyebath is rendered colourless. Many colouring matters are taken up by animal fibres more readily from an acid than from a neutral bath; and in such cases the bath is usually acidified by sulphuric, acetic, formic, lactic, or tartaric acid. If sulphuric acid be used, sodium sulphate is generally added also. Some dyers add acid sodium sulphate as such, instead of forming it in the dye-bath. In wool-dyeing, sodium or magnesium sulphate is often added to the bath possibly to reduce the solubility of the colouring

matter and to obtain faster and more even colours. In some cases, as when wool is dyed with alkali-blue or cotton with indigo, a colourless neutral substance is absorbed by the fibre, and is only converted into a coloured compound by a subsequent chemical action, namely, the liberation of the free sulphonic acid in the first case and oxidation to indigo-blue in the latter.

The **"ingrain colours"** produced on cotton by means of primuline and other compounds afford a remarkable example of the building up of a dye within the fibre.

Unmordanted cotton is not dyed by the ordinary basic dyestuffs or acid wool dyestuffs, but is dyed by the direct cotton or "salt" dyestuffs which are mainly derivatives of tetrazotised benzidine and derivatives; it is also dyed from alkaline liquids containing reducing agents in presence of air, by indigo and its derivatives, and by other vat-dyestuffs such as indanthrene. During recent years the sulphide dyestuffs have come into great prominence; these dye unmordanted cotton from a bath containing alkaline sulphides in solution, with the help of atmospheric oxygen.

Adjective Dyes.—In many cases, cotton and other vegetable fibres can only be dyed through the intervention of a mordant. Sometimes the mordant acts by forming an insoluble compound with the colouring matter, according to a definite chemical action; and in other cases it simply serves as a medium on which the colour is adsorbed. In some cases, colouring matters which have themselves been fixed on the fibre act as mordants for others. Thus the benzidine dyes may be employed for mordanting the basic aniline dyes on cotton. Several useful combinations are thus obtainable.

The proteins resemble silk and wool in their affinity for coal-tar dyes, and hence albumin, etc., are employed in calico-printing. A solution of albumin mixed with the colouring matter is printed on the cotton fibre. On steaming, the albumin is coagulated and the colour becomes fixed.

Tannin acts as a mordant for basic dyes, as it forms with them insoluble tannates.[1] These compounds are soluble in acetic acid or

[1] The tannates of the colour-bases may be either soluble or insoluble, according to the proportions used, the following being the quantities required to form insoluble lakes, according to J. Koechlin:

	Dye	Tannic acid	Sodium carbonate crystals
Magenta	4	5	2
Malachite green	4	5	1
Parma	4	5	1
Methyl green	4	10	4

alcohol, and if the solutions thus obtained are thickened with starch or dextrin and printed on cotton, the tannate becomes fixed and insoluble on steaming the goods. Better results are obtained by employing in conjunction with the tannin and colour-base a metallic salt (*e. g.*, tartar emetic, stannic chloride, lead acetate, etc.) capable of yielding an insoluble tannate.

The use of oils in dyeing turkey-red is a familiar example of the application of oil mordants, which are generally employed in conjunction with inorganic mordants. This class includes the so-called soluble oil.

The acetates of iron (ferric), aluminium, and some other metals undergo decomposition when heated, with formation of free acetic acid and insoluble basic acetates. Hence these metallic acetates act as valuable mordants, especially for silk; they also become perfectly fixed on cotton by steaming. The thiocyanates have recently come into use for a similar purpose.

Wool is usually mordanted with chromium or aluminium compounds; the former are obtained by the use of alkali dichromate in conjunction with tartaric, sulphuric, oxalic, or lactic acid, or of chromium fluoride. Other salts also have been used.

Classification of Dyes and Colouring Matters.

The arrangement of dyes and colouring matters in groups with a view to their convenient description is preferably based on their chemical characters. In certain cases, however, the dyes defy simple classification, and in others a strict adherence to a system is inconvenient. The colouring matters still obtained from natural sources are also best considered together in the same section, however they may vary in chemical nature.

In the following section certain dyes of these groups are considered individually, but the text-books which deal exhaustively with these dyes must be consulted if for any reason a full list is required. Before doing this, however, the section dealing more directly with the analysis of dyes may be consulted (see page 513).

The following arrangement is that adopted in this work for the description of the dyes and colouring matters and the methods of recognising them:

1. Nitro-, nitroso-, and isonitroso-dyestuffs.
2. Azoxy-dyestuffs.

3. Pyrazolone-dyestuffs.
4. Azo-, and tetrazo-dyestuffs.
5. Oxyketone dyestuffs.
6. Di- and triphenylmethane dyestuffs.
7. Pyrone, xanthone, and fluoran dyestuffs.
8. Indamines and indophenol dyestuffs.
9. Azine dyestuffs.
10. Oxazine and thiazine dyestuffs.
11. Quinoline and acridine dyestuffs.
12. Thiazole and sulphur dyestuffs.
13. Natural dyestuffs.
14. Examination and analysis of dyestuffs.
15. Examination of dyed fabrics.

1. Nitro-, Nitroso-, and Isonitroso-colouring Matters.

Of this class, the nitro-colouring matters are the most numerous and also the most important; the other two groups of this class yield but a few unimportant dyestuffs.

(a) Nitro-compounds.

Nitro-compounds contain one or more nitryl radicles (NO_2) in place of the hydrogen of the original substance. They are crystalline compounds, usually more or less yellow in colour, only slightly soluble in cold water, and not soluble to any great extent in boiling water; but they are readily soluble in alcohol and ether, and are removed by the latter solvent from their acidified aqueous solutions.

The nitrophenols and their allies have marked acid properties, readily decomposing metallic carbonates, and furnishing a series of salts all or nearly all of which are more or less soluble in water, and often form crystals of great beauty, ranging in colour from a pale yellow to a fine crimson. The salts of the nitro-phenols and their allies all deflagrate with greater or less facility when ignited, and many of them detonate on percussion, the more highly nitrated compounds (*e. g.*, the picrates) exploding with considerable violence.

In cases where the nitro-compound is the product of a limited nitration, it may be converted into the corresponding sulphonic acid by strong sulphuric acid; but this is not possible when, as in the case of picric acid, the number of nitro-groups in the molecule is the maximum. With the exception of Flavaurin, Naphthol Yellow S, and

Schoellkopf's Brilliant Yellow, none of these dyestuffs are sulphonated compounds. The sulphonic acids of the nitro-colouring matters are stable substances, readily soluble in water. The nitro-colouring matters as a class dye wool and silk yellow or orange, but have no affinity for cotton. Their acid characters are well marked and stronger than those of the phenolic compounds from which they are derived. They dissolve in concentrated sulphuric acid to form yellow or colourless solutions. Strong reducing agents, such as stannous chloride and hydrochloric acid, convert them into the colourless amino-derivatives. Phosphine is turned yellow by ammonia and is extracted from its alkaline aqueous solutions on agitation with ether, but the nitro-compounds are not dissolved by ether under similar conditions. In presence of dilute sulphuric acid in excess, the simple nitro-dyes (*e. g.*, picric acid, dinitrocresol, dinitronaphthol, and aurantia) are extracted by ether, but the sulphonic acids (*e. g.*, Naphthol Yellow S) are not dissolved, in this respect resembling the sulphonated yellow azo-dyes.

The nitro-colours are sold in the form of their alkali salts; picric acid, however, is an exception, being sold in the free state owing to the explosive nature of the picrates.

The nitro-dyestuffs produce yellow to orange yellow colours when dyed on the animal fibres; they have no application in cotton dyeing. As a class their use is gradually decreasing, although the Naphthol Yellows and Brilliant Yellow still appear to maintain a certain prestige.

Commercial name	Formula	Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
			With sodium hydroxide	With hydrochloric acid	With strong acid	On dilution with water	
Picric acid.	$C_6H_2\left\{\begin{matrix}(1)OH\\(2)NO_2\\(4)NO_2\\(6)NO_2\end{matrix}\right.$	Yellow crystals; yellow solution.					Soluble in alcohol. With KCN—brown sol.
Victoria Yellow.	$C_6H_2\left\{\begin{matrix}(1)OK\\(2)CH_3\\(3,5)(NO_2)_2\end{matrix}\right.$ and $C_6H_2\left\{\begin{matrix}(1)OK\\(4)CH_3\\(3,5)(NO_2)_2\end{matrix}\right.$	Orange powder; orange solution.	No change.	White pp.	Pale yellow.		Used for colouring foods.
Naphthol Yellow.	*(Acid)* $C_{10}H_5\left\{\begin{matrix}(1)OH\\(2)NO_2\\(4)NO_2\end{matrix}\right.$	Orange yellow plates; yellow solution.		Precipitates dinitronaphthol.			Soluble in alcohol.
Naphthol Yellow S.	$C_{10}H_4\left\{\begin{matrix}(1)ONa\\(2)NO_2\\(4)NO_2\\(7)SO_3Na\end{matrix}\right.$	Orange yellow powder; yellow solution.	Yellow pp.	Yellower.			
Brilliant Yellow.	$C_{10}H_4\left\{\begin{matrix}(1)OH\\(2)NO_2\\(4)NO_2\\(8)SO_3Na\end{matrix}\right.$	Yellow powder; yellow solution.	Orange pp.	Clear yellow solution.	Pale yellow.		
Aurantia.	$N(NH_4)\left\{\begin{matrix}(2)C_6H_2\left\{\begin{matrix}(1)NO_2\\(3)NO_2\\(5)NO_2\end{matrix}\right.\\(2)C_6H_2\left\{\begin{matrix}(1)NO_2\\(3)NO_2\\(5)NO_2\end{matrix}\right.\end{matrix}\right.$	Brown crystals; orange solution.		Yellow pp.			
Nitrosamine red.	$C_6H_4\left\{\begin{matrix}(1)N<\begin{matrix}NO\\Na\end{matrix}\\(4)NO_2\end{matrix}\right.$ or $C_6H_4\left\{\begin{matrix}(1)N=N.ONa\\(4)NO_2\end{matrix}\right.$	Yellow paste; yellow solution.		Yellow pp.			

The following sections contain detailed descriptions of the principal nitro-colouring matters.

Picric Acid.—2:4:6—Trinitrophenol. Trinitrophenol.

$$C_6H_3N_3O_7 = C_6H_2\left\langle\begin{matrix}OH\\(NO_2)_3.\end{matrix}\right.$$

Picric acid is fully dealt with in Vol. 3 under *Explosives*. The following information may be regarded as supplementary to that given in Vol. 3.

Solubility.—J. Bougnault (*J. Soc. Chem. Ind.*, 1903, **22**, 1019; *J. Pharm. Chim.*, **18**, 116) states that picric acid is not very soluble in dry ether, though in moist ether its solubility is greater. Ether of sp. gr. 0.721, dried over calcium chloride, dissolved 10.8 grm. of picric per litre at 13°, while a sample of sp. gr. 0.725, containing 0.8% of water, dissolved 36.8 grm. per litre, and one containing 1% of water 40 grm. per litre. The solution in dry ether is practically colourless.

Detection.—According to H. Svoboda (*Zeit. Anal. Chem.* 1897, **36**, 513) a cold aqueous solution of picric acid gives with Methylene Blue solution a flocculent violet precipitate soluble in ether, chloroform and hot water to solutions the colour of which varies from blue to green. On evaporating the chloroform solution to dryness a violet residue is obtained.

Estimation of Picric Acid.

In addition to the method of titration given in Vol. 3, free picric acid may also be titrated by taking advantage of its power of liberating iodine from a solution containing potassium iodide and iodate; in this respect it acts as a monobasic acid and each c.c. of N/10 thiosulphate solution is equivalent to 0.229 grm. of picric acid. The liberated iodine is titrated in the usual manner with thiosulphate solution, using starch paste as indicator; the picric acid in picrates may be estimated by acidifying with hydrochloric acid, extracting with benzene, evaporating the extract and dissolving the residue in water; this solution is then titrated as above (E. Feder, *Analyst*, 1906, **31**, 368).

M. Busch and G. Blume (*Z. angew. Chem.*, 1908, **21**, 354) estimate picric acid by means of Nitron, the well-known quantitative reagent for nitrates, 1.4-diphenyl, 3.5-endanilodihydrotriazole,

$$\begin{matrix} & \diagup NPh \diagdown & \\ CH & —NPh.N & =C \\ & \diagdown NPh \diagup & \end{matrix}$$

Nitron picrate is practically insoluble in water. About 150 c.c. of a solution of the substance containing not more than 1 grm. of picric acid per litre, are acidified with 1 to 2 c.c. of dilute sulphuric acid, heated to boiling and treated with 10 c.c. of a 10% solution of nitron in 5% acetic acid. The reagent is added slowly. After cooling the lemon-yellow needles of nitron picrate are collected in a Neubauer crucible, washed with 50–100 c.c. of cold water, and dried for 1 hour at 100°. Equal molecules of the nitron and picric acids are combined in the precipitate and the weight obtained must therefore be multiplied by $\frac{229}{541}$ in order to convert it into weight of picric acid. When necessary alcohol may be used for solution. In presence of hydrobromic, hydriodic, chloric. perchloric, nitrous, nitric or chromic acids the method is inapplicable.

Nitrosamine Red[1] (see Table, p. 122).

Nitrosamine red comes into commerce in the forms of a yellow paste, which forms a yellow solution with water. On the addition of acids to the aqueous solution the free *p*-nitrophenylnitrosamine is precipitated. The latter is gradually converted by an excess of acid into a salt of a diazo-derivative of nitro-benzene. Nitrosamine red is dyed on cotton with β-naphthol, giving brilliant red shades (Paranitraniline Red) and much used in practice.

The **Mikado golden yellows** or **Direct Yellows** are condensation products of *p*-nitrotoluenesulphonic acid. They occur in the form of yellow powders, yielding a yellow solution in water, and are insoluble in alcohol. The addition of sodium hydroxide to the aqueous solutions produces a yellow precipitate, whereas hydrochloric acid gives a brown colour. Strong sulphuric acid dissolves the dyestuff with an orange colour, which changes to yellow on dilution with water. These dyestuffs yield satisfactory colours on cotton, which they dye directly. The shades produced are very bright yellows which possess good fastness to washing, acids and alkalies, and are fairly fast to light. These dyestuffs may also be employed for dyeing animal fibres, being dyed from a neutral or slightly acid bath. The shades produced are fast to washing but are considerably altered by both acids and alkalies.

[1] *Ber.*, 1894, 27, 514.

Nitronaphthols.

The two modifications of naphthol, $C_{10}H_7.OH$, yield on nitration compounds analogous to those obtained by similar means from phenol and cresol (see also Vol. 3). The dinitro-derivative of α-naphthol is the most important.

2:4-Dinitroalphanaphthol, $C_{10}H_5(NO_2)_2.OH$.

Dinitronaphthol forms yellow needles, melting at 138°, and somewhat readily volatile. It is nearly insoluble in water, but soluble in alcohol and ether. It closely resembles picric acid, and forms a series of beautiful and well-crystallised salts yielding golden yellow solutions, which are decolourised by hydrochloric acid, a yellowish-white precipitate of the free nitronaphthol being produced, soluble in either. Ammonia is without action. Potassium and sodium hydroxides produce orange-red precipitates in strong solutions. Potassium cyanide and ammonium sulphide react as with picric acid.

The *sodium salt* of dinitronaphthol forms readily soluble glistening needles containing $C_{10}H_5(NO_2)_2.ONa + H_2O$, and deflagrates when heated. The *ammonium salt* burns quietly when heated, and is soluble in alcohol. The *calcium salt* forms yellowish-red crystals of the formula $[C_{10}H_5(NO_2)_2O]_2Ca + 6H_2O$.

The potassium, sodium, ammonium, and calcium salts of dinitronaphthol have been extensively employed as colouring matters under the name of

Naphthol Yellow; MANCHESTER YELLOW; NAPHTHYLAMINE YELLOW; MARTIUS' YELLOW; GOLD YELLOW. This dyestuff occurs as an orange powder or crystals only sparingly soluble in water, though readily soluble in alcohol. On the addition of hydrochloric acid to the aqueous solution dinitroalphanaphthol is liberated as a light yellow precipitate. Sulphuric acid gives a yellow solution in which a light yellow precipitate is formed on dilution with water. In an acid bath this substance dyes silk and wool (but not cotton) a brilliant yellow colour, free from the greenish reflection peculiar to fabrics dyed with picric acid. Owing to the volatile nature of dinitronaphthol (which is liberated by the acid of the bath), the colour marks and rubs off, and hence the employment of Naphthol yellow as a dye has diminished.

Naphthol Yellow is occasionally adulterated with *dextrin* and *sodium sulphate*, the proportion of the latter admixture sometimes reaching 50%. It is sometimes adulterated with *picric acid*, to detect which a sample should be dissolved in water, the cold solution acidified freely with hydrochloric acid, and the liquid filtered. If picric acid be present the filtrate will have a marked yellow colour, and the acid can be obtained in crystals by evaporation.

Naphthol Yellow may be distinguished from picric acid by boiling wool in the acidified solution, washing it, heating it with cuprammonium sulphate, and again washing. When a fibre or fabric dyed with picric acid is boiled with the ammoniacal copper solution it turns bluish-green, but if Naphthol Yellow has been used an olive-green tint results.

When a material dyed with Naphthol Yellow is wrapped in white paper and heated to 120° in an air-bath, part of the yellow colour is transferred to the paper. Hot water or hot dilute ammonia dissolves out the colouring matter, and the yellow solution is decolourised by hydrochloric acid, a yellow-white precipitate being produced (distinction from picric acid).

Naphthol Yellow has sometimes been employed for colouring butter, cheese, macaroni, mustard, saffron, etc., for which applications its marked poisonous characters render it very unfit.[1] The detection of butter-colours will be described under "Annatto" (see also p. 624).

Martius' yellow when used in foods taken into the stomach may be detected in the urine by the following methods:

1. The urine slightly acidified with hydrochloric acid is shaken up with ether. A portion of the ethereal layer is shaken with potassium hydroxide solution. The alkaline liquid is acidified with hydrochloric acid and warmed with some strands of white wool free from fat and mordanted with alum. The wool is coloured yellow in the presence of as little as 0.000001 grm. of the dyestuff.

2. A portion of the ethereal solution is evaporated to dryness, and a drop of potassium cyanide solution is added to the residue, when a red colouration is obtained.

1 Comparatively small doses of Naphthol Yellow are said to cause asthmatic breathing, a considerable rise of temperature (without convulsions), and ultimately death (Cazeneuve and Lépine, *Comp. rend.*, 1885, 1167). According to Weyl (*Ber.*, 1888, 21, 2191), Martius' yellow is well tolerated by rabbits, but small doses proved fatal to dogs. A dog weighing 6850 grm., to which a dose of 0.5 grm. of dinitronaphthol was given on 2 successive days, and 1 grm. of the sodium salt on the third day, died on the fourth day. Less than 1 grm. given subcutaneously caused the death of a similar dog. On the other hand, Naphthol Yellow S proved innocuous to dogs in 4 times these amounts.

3. Another portion of the residue by evaporation of the ethereal solution is mixed with potassium bisulphate, heated to redness in a glass tube, and the residue dissolved in water. A paper moistened with Guess's reagent and placed in the solution is coloured violet.

4. A solution of Martius' yellow, or urine containing it, gives with cobalt chloride and a little sodium hydroxide, a fine green pigment.

5. With stannous chloride and a trace of ammonia, Martius' yellow gives a white precipitate, which becomes rose-red on subsequent treatment with ammonia.

For the recognition of Martius' yellow in the stomach, intestines, etc., these are finely cut up, acidified slightly with hydrochloric acid, and digested for some hours at 40°–50° with absolute alcohol. The liquid is filtered, evaporated at a low temperature, made alkaline with potassium hydroxide, filtered, acidified with hydrochloric acid, and shaken out with ether, which solution is then examined as above.

2:4-Nitronaphthol-sulphonic Acids.

When α-naphthol is warmed with excess of fuming sulphuric acid it yields a trisulphonic acid, which on subsequent treatment with strong nitric acid yields, on cooling, crystals of

2:4-Dinitro-α-naphthol-sulphonic acid, $C_{10}H_4(SO_3H)(NO_2)_2$-OH. The product is purified by recrystallisation. It forms long yellow needles, readily soluble in warm water, but insoluble in ether. These characters distinguish it from picric acid, dinitro-naphthol, etc. Its salts are easily crystallisable, said to be non-poisonous, and dye wool and silk (but not cotton) a bright yellow colour, which is fast to light, non-volatile, and does not mark or rub off. For these reasons the salts have replaced picric acid and the dinitro-naphtholates.

Potassium dinitro-α-naphthol-sulphonate, $C_{10}H_4(SO_3K)(NO_2)_2$.OK, forms as an orange-yellow precipitate on mixing a strong solution of the free acid with one of potassium sulphate. It is sparingly soluble in cold, but readily in hot water. By boiling it with strong hydrochloric acid the free acid, or, according to some, a *salt*, $C_{10}H_4$-$(SO_3K)(NO_2)_2OH$, is formed.

The sodium and ammonium salts of dinitronaphthol-sulphonic acid are freely soluble, but the *barium* and *lead* salts only sparingly so.

The *salts* of dinitronaphthol-sulphonic acid are yellow or orange.

On heating, they swell up and emit sparks, but do not deflagrate. The solutions are yellow or brownish-yellow, becoming pale yellow on adding hydrochloric acid, but no precipitate is produced, and the diluted acid liquid is not decolourised by agitation with ether. (Distinction from picric acid, etc.) With sodium hydroxide an orange-yellow precipitate is formed, soluble on warming. In strong sulphuric acid the dinitronaphthol-sulphonates dissolve with pale yellow colour. In other reactions they resemble Manchester yellow, but do not volatilise or colour their paper envelope at 120°.

Naphthol yellows; Citronin;[1] **Acid Yellow S; Brilliant Yellow,** etc., are names given to the potassium, sodium, ammonium, and calcium salts of dinitronaphthol-sulphonic acid. The free acid is also met with under the name of "Naphthol Yellow" (Levinstein).

Commercial Naphthol Yellow S varies much in character. Some qualities are practically pure, while others contain sodium sulphate and chloride in notable quantity. C. Rawson (*J. Soc. Dyers*, 1888, **4**, 82) has proposed a method of assay depending on the precipitation of the colouring matter by a solution of Night Blue, which is made by dissolving 10 grm. in 50 c.c. of glacial acetic acid, and diluting the liquid to 1 litre. The Naphthol Yellow is used as a solution containing 1 grm. per litre. The latter solution is added to 10 c.c. of the former until on filtration of a portion of the liquid it is found to have a faint yellow colour. The method is similar to that described for the determination of picric acid. Two molecules of Night Blue react with one of Naphthol Yellow.

Naphthol Yellow S may be adulterated with the cheaper Naphthol Yellow, and the latter may be detected by adding hydrochloric acid to the aqueous solution; Naphthol Yellow is precipitated or the solution becomes milky; whereas a solution of pure Naphthol Yellow S remains clear. If the dry colour is treated with ether, Naphthol Yellow S will not colour the liquid even on addition of sodium hydroxide, while Naphthol Yellow colours the ether yellow and remains yellow on addition of sodium carbonate.

Nitro-diphenylamines.

On treating diphenylamine with nitric acid it readily yields nitro-substitution products. The tetranitro-derivative, $[C_6H_3(NO_2)_2]_2NH$,

1 The name citronin is used both for Naphthol Yellow S and the product obtained by acting with nitric acid on diphenylamine, as also for the azo-dye called azoflavin.

mixed with a little of the dinitro-product, forms the colouring matter known as "Citronin." On warming diphenylamine or methyl-diphenylamine with nitric acid, it yields hexanitro-diphenylamine, a substance of strongly acid character, m. p. 238°, the *ammonium salt* of which constitutes the "aurantia" of commerce.

Aurantia, or *Imperial yellow* $[C_6H_2(NO_2)_3]_2.N(Na)$, forms a reddish-yellow crystalline powder, or brownish-red crystals which decrepitate on heating and sometimes deflagrate slightly. Aurantia is easily soluble in water forming a solution which is red when concentrated, but yellow when diluted. On addition of hydrochloric acid, the aqueous solution yields a sulphur-yellow flocculent precipitate of free hexanitro-diphenylamine, and on filtering a nearly colourless liquid is obtained. The precipitate dissolves on agitation with ether. An acid solution of stannous chloride also precipitates the free acid, but the yellow precipitate becomes dark brown on boiling. Copper salts also turn the solution of Aurantia brown. Solutions of Aurantia are darkened or reddened by alkali hydroxides, and if concentrated a dark red precipitate is produced. Solid Aurantia is not changed in colour by strong sulphuric acid.

Aurantia does not appear to be entirely harmless in its physiological action, as even dilute solutions of the dyestuffs produce painful blisters on the skin. There seems to be an isomeric hexanitrodiphenylamine which is harmless.

On the fibre, hydrochloric acid turns the colour due to aurantia a lighter yellow. Ammonia and sodium hydroxide produce but little change. The dark brown colouration produced on warming with stannous chloride is the most characteristic reaction of aurantia.

Aurantia has been almost completely replaced by the azo-colours.

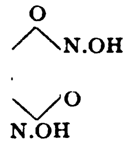
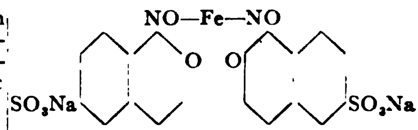
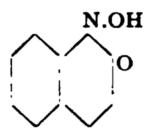
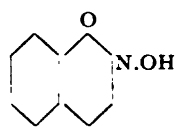
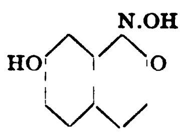
(b) Nitroso- and Isonitroso-colouring Matters.

By treating an aqueous solution of phenol with potassium nitrite and acetic acid, a compound is formed which was formerly supposed to be nitroso-phenol, $C_6H_4(NO).OH$, but which also behaves as the isodynamic quinoneoxime, $C_6H_4.O(NOH)$.

The *o*-quinoneoximes dye on metallic mordants, while the other quinoneoximes do not. These colours are permanently decolourised by the action of reducing agents, aminophenols being formed. The

nitroso-compounds are dyed almost exclusively on iron mordants, invariably giving green shades with this metal which are notable for their great fastness to light. Brown shades are obtained by the use of cobalt mordants.

The following table shows the nitroso- and iso-nitroso-colours:

Commercial name	Chemical name	Constitutional formula
Dinitrosoresorcinol. Resorcin Green. Dark Green. Solid Green. Chlorin. Russian Green. Alsace Green. Fast Myrtle Green.	Dinitrosoresorcinol. Diquinonedioxime.	
Naphthol Green B.	Ferrous-sodium salt of nitroso-β-naphthol-β-monosulphonic acid.	
Nitrosonaphthol. Gambin Y. Alsace Green J.	α-Nitroso-β-naphthol.	
Gambin R.	β-Nitroso-α-naphthol.	
Dioxin. Gambin B.	Mononitroso-dihydroxynaphthalene.	

Dinitrosoresorcinol, $C_6H_2O_2(NOH)_2$.—This compound, which forms the commercial colouring matter known as *Resorcin Green* or *Solid Green*, is obtained in a manner similar to quinoneoxime, substituting resorcinol for phenol. It forms yellowish-brown or green plates, or a greyish-brown powder. The commercial product is sold as a dark grey paste, as the dry powder is said to be explosive. It dissolves with difficulty in cold water, but readily in hot. It deflagrates slightly when heated to 115°. Dinitrosoresorcnol has acid characteristics. It decomposes carbonates and to some extent acetates, and forms a series of alkali-metal salts, of which the normal are soluble, and the acid salts, of the type $C_6H_2O_2(NOH)(NONa)$, are sparingly soluble, green, crystalline powders.

By the action of resorcinol and sulphuric acid on dinitrosoresorcinol, Azoresorufin is formed, a substance which is analogous with the Liebermann's dye-stuff obtained in a similar manner from phenol.

Naphthol Green B is the sodium-ferrous salt of a nitroso-β-naphtholsulphonic acid. It forms a dark green powder, which leaves, on ignition, a residue containing iron and sulphides. The colouring matter dissolves in water with yellowish-green colouration, the solution being unchanged by hydrochloric acid, but rendered bluish-green by alkalies. In concentrated sulphuric acid, Naphthol Green dissolves with a yellowish-brown colour, the solution becoming yellow on dilution, and then giving a blue colouration or precipitate both with ferro- and ferricyanides.

Gambin Y, α-nitroso-β-naphthol, is an olive-green paste, slightly soluble in water with a yellow colour, the solution remaining unaltered by hydrochloric acid; sodium hydroxide produces a greenish-yellow fluorescence. It is soluble in alcohol, giving an orange solution. In concentrated sulphuric acid it dissolves to a dark brown solution which gives a flocculent precipitate on dilution with water.

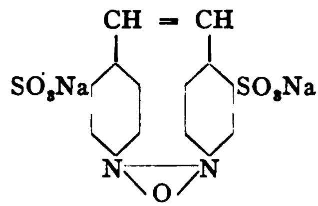
Gambin R, β-nitroso-α-naphthol is isomeric with the above.

Dioxin is produced by the action of nitrous acid on (2 : 7) dihydroxynaphthalene. It is a reddish-brown paste, very sparingly soluble in water, but dissolving in sodium hydroxide solution with an intense brown colour; also soluble in alcohol, giving an orange solution. With concentrated sulphuric acid a green solution is obtained, which yields a red precipitate on dilutiou with water.

2. Azoxy-colouring Matters.

Sun Yellow.—Curcumin S.

This dyestuff is also sold under the names of Jaune Soleil and Maize, and has the formula:



It is, therefore, the sodium salt of azoxy-stilbenedisulphonic acid.

Curcumin S is produced by the action of sodium hydroxide on *p*-nitrotoluenesulphonic acid. It is a brown powder soluble in water, giving a brownish-yellow solution. With sulphuric acid it gives a violet solution which changes to yellow on dilution with water. Hydrochloric acid gives a brown precipitate from the aqueous solution; sodium hydroxide an orange precipitate.

Direct Yellow G is the sodium salt of dinitrosostilbenedisulphonic acid.

It is a brown powder, soluble in water with an orange colour. The addition of sodium hydroxide to the aqueous solution produces a yellow precipitate, as also does hydrochloric acid. It dissolves in strong sulphuric acid with a red colour, which changes to yellow on dilution with water.

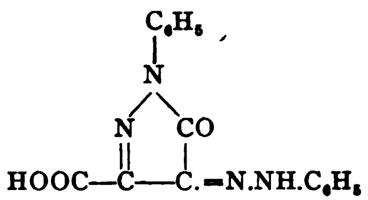
Mikado Oranges, G, R, 2 R, 3 R, 4 R, and **5 R,** and **Mikado Yellow** are prepared by boiling *p*-nitrotoluene-sulphonic acid with alkalies in the presence of certain reducing agents, such as glucose. They occur as orange powders, soluble in water giving an orange solution. On the addition of hydrochloric acid to the aqueous solution a brown precipitate is produced; sodium hydroxide gives a yellow precipitate. Strong sulphuric acid dissolves the dyestuff to a blue solution, which gives a brown precipitate on dilution with water.

Mikado Brown, B, 3 GO and **M,** are dyestuffs produced in a similar manner to the above. They are brown powders, giving a brown solution in water. Sodium hydroxide with the aqueous solution produces but a very slight precipitate; hydrochloric acid gives a brown

precipitate. Strong sulphuric acid dissolves the dyestuff to a dark red solution, which gives a brown precipitate on dilution with water.

3. Pyrazolone Colouring Matters.

Tartrazin is prepared by the action in alkaline solution of phenylhydrazine-sulphonic acid on dihydroxytartaric acid. According to Nietzki, tartrazin has the following constitution:



being a derivative of pyrazolone. It forms an orange-yellow powder, soluble in hot water to a golden-yellow solution, which if concentrated deposits a yellow precipitate on cooling. On adding alcohol to the concentrated aqueous solution a crystalline precipitate is obtained. The solution is not changed by dilute acids, but becomes reddish on adding sodium hydroxide. Stannous chloride produces a yellow precipitate, soluble in oxalic acid. Barium chloride gives a yellow precipitate, but calcium chloride occasions no change. Concentrated sulphuric acid dissolves the solid dye with a yellow colour, which is unchanged on dilution. Tartrazin precipitates the coal-tar bases very completely,[1] and dyes wool yellow in an acid bath. This is the only dye of this class which has come into use.

4. Azo- and Tetrazo-colouring Matters.

The azo-compounds in general are acid-dyeing colours and are produced by combining diazotised aromatic amines and their sulphonic acids with aromatic amines or phenols and their sulphonic acids.

Diazobenzene chloride solution is prepared by slowly adding the calculated quantity of sodium nitrite solution to a solution of aniline hydrochloride containing at least 1.5 equivalents of free hydrochloric

[1] W. R. Richardson, *Jour. Soc. Dyers and Col.*, 1887, 3, 2.

acid, and kept at a temperature of about 4° by the addition of ice. The action is finished when the presence of excess of nitrous acid, as shown by the blue colour produced by the liquid on starch-iodide paper, persists for 2 or 3 minutes. This test is commonly used for the titration of aniline oil and salt, and a standardized diazobenzene solution produced in this way may be employed for the titration of amines and phenols which are used in the production of azo-dyestuffs. Diazobenzene solution is unstable and rapidly decomposes at the atmospheric temperature.

p-Diazobenzene-sulphonic Acid, $C_6H_4\begin{matrix}.N: \\ .SO_3.\end{matrix}:N.$ Diazosulphanilic acid. This substance is not well named, as it is really the anhydride of the true sulphonic acid, $C_6H_4(SO_3H).N_2.OH$. The diazosulphonic acid forms white crystals, insoluble in cold water but readily soluble at 60°–70°. It is decomposed by water at a higher temperature, with formation of para-phenolsulphonic acid, while boiling alcohol converts it into benzene-sulphonic acid, $C_6H_5.SO_3H$.

Caution should be used in handling the dry substance as it occasionally explodes violently through quite inconsiderable causes, such as attempts to break up the crystals with a glass rod.

Aniline Yellow, $C_6H_5.N_2.C_6H_4.NH_2,HCl$, also called *Spirit-Yellow*, is the hydrochloride of amino-azobenzene, and can be obtained by mixing dilute aqueous solutions of diazobenzene chloride and aniline. In the pure state it forms bluish-violet, lustrous needles, dissolving in water with a yellow colour which is turned to a fine red by acids. In strong sulphuric acid it dissolves with a brown colour, becoming red on dilution. On heating the aqueous solution of aniline yellow, the free base is precipitated. Free amino-azobenzene is also completely precipitated from its salts by ammonia, and may then be taken up by agitation with ether. In the pure state it forms yellow crystals, which melt at 120° and volatilise unchanged. It is insoluble in water, but soluble in alcohol. From acid solutions it dyes silk red, the salt itself being taken up, but on washing with water the salt is decomposed and the base imparts a yellow colour to the fibre. Aniline yellow is not fast, and easily volatilises when the fibre is steamed. Hence it is not now used as a dye, but forms the starting-point in the manufacture of other aniline colours and of indulines.

Chrysoïdine, $C_6H_5.N_2.C_6H_3(NH_2)_2.HCl$, is the hydrochloride of diamino-azobenzene. It is formed when an aqueous solution

of metaphenylenediamine is poured into a very dilute solution of diazobenzene chloride. It usually occurs in the form of a reddish-brown crystalline powder, or blackish-green or dark violet crystals having a metallic reflex. It is soluble in boiling water and absolute alcohol. The hot concentrated solution forms a gelatinous blood-red mass on cooling. The brown or orange-coloured aqueous solution is turned red by excess of hydrochloric acid, dyes wool orange-yellow, and gives with alkalies a bright yellow precipitate of the free base, m. p. 117.5°, and slightly soluble in water, readily in alcohol and ether. Strong sulphuric acid dissolves chrysoïdine with reddish-brown or orange colour, which turns almost scarlet on heating (distinction from phosphine) and cherry-red on dilution.

Dimethyl-amino-azobenzene, $C_6H_5.N_2.C_6H_4.N(CH_3)_2$, sometimes called *Butter Yellow*, is the dimethyl-derivative of Aniline Yellow. When pure, it crystallises in small yellow plates, m. p. 115°, and its hydrochloride forms long, slender purple-red needles. It is insoluble in water, but dissolves with red colouration in hydrochloric acid, from which sodium hydroxide throws down an orange-yellow precipitate of the base; soluble in strong sulphuric acid with a yellow colour, turning red on dilution. Its alcoholic solution has been recommended by B. Fischer (*Analyst*, 1885, **10**, 152) as an indicator in alkalimetry, in preference to methyl orange, which is the ammonium salt of its sulphonic acid. It is chiefly used for colouring butter and oils.

Hydroxy-azo-compounds.

***m*-Dihydroxy-azobenzene**, or **resorcinol-azo-benzene**, $C_6H_5.N_2.C_6H_3(OH)_2$. This substance forms red needles, m. p. 168°, and is readily soluble in alcohol. In commerce it occurs as a brown powder under the name of *Soudan G*. It is slightly soluble in hot water, with yellow colour, the solution giving a bright brown precipitate with hydrochloric acid. In alkalies it is soluble with brown colour, and with concentrated sulphuric acid it yields a yellowish-brown solution, giving a brown precipitate on dilution. It has been used for colouring oils and varnishes.

The acid potassium and sodium salts of the sulphonic acid of resorcinol-azobenzene occur in commerce under the name of *Chyrsoïn*, *Tropæolin O* or *R*, etc.

β-**Naphthol-azo-benzene,** $C_6H_5.N_2.C_{10}H_6.OH\beta$. Under the name of *Soudan I*, it enters into commerce as a brick-red powder, insoluble in water, but soluble in alcohol with yellow colour. Concentrated sulphuric acid dissolves it with magenta-red colour; and on dilution the solution gives an orange-yellow precipitate. It is chiefly employed for colouring oils and varnishes.

The sodium salt of the corresponding sulphonic acid forms the colouring matter known as *Crocein Orange* or *Ponceau* 4 *BG*.

Soudan II is homologous wth Soudan I.[1] It is also called *Red B*, and is used for colouring oils and varnishes. It is insoluble in water, but soluble in alcohol with an orange colour. It dissolves in concentrated sulphuric acid to a magenta-red solution, which gives a pale yellow precipitate on dilution with water.

α-**Naphthol-azo-naphthalene,** $C_{10}H_7.N_2.C_{10}H_6.OH\alpha$, occurs in commerce under the name of *Soudan Brown* or *Pigment Brown*. It is an insoluble brown powder, dissolving sparingly in dilute alkalies. In concentrated sulphuric acid it dissolves with blue colouration, a brown precipitate being produced on dilution with water. It is soluble in alcohol, and is used for colouring soaps and oils.

Azarin S is a compound of dichlorphenolazo-*β*-naphthol with ammonium bisulphite. It is a yellow paste, smelling of sulphurous acid; it dissolves sparingly in water with a yellow colour, the solution giving with sodium hydroxide a violet precipitate, and with hydrochloric acid an orange precipitate. The dye dissolves in strong sulphuric acid with a magenta red colour, the solution giving a brown precipitate on dilution with water. It has been chiefly employed in calico-printing, and its shades are very fast to soap and fairly so to light.

Sulphonated Azo-compounds.

The amino- and hydroxy-derivatives of azobenzene and its analogues have marked dyeing properties, but owing to their slight solubility in water it is found convenient to sulphonate them. This is effected by treatment with fuming sulphuric acid; or, instead of sulphonating after diazotising, the aniline or other amine is first sulphonated and then diazotised, and the diazo-sulphonic acid formed is then caused to

[1] Soudan III is the commercial name of a colouring matter of the tetrazo-class (see page 162).

react with other amines or phenols, according to the character of the dye required. In this manner sulphanilic acid, $C_6H_4(SO_3H).NH_2(1:4)$[1] and naphthionic acid, $C_{10}H_6.SO_3H.NH_2[1:4]$, form the starting-points of important series of azo-colouring matters. When diazotised, these two compounds are converted respectively into diazobenzene sulphonic acid and diazonaphthalene-sulphonic acid. By the action of the former of these on aniline, *Acid Yellow* is obtained, while with dimethyl-aniline *Helianthin* is the product. With phenol in alkaline solution, the sodium salt of phenyl-diazobenzene-sulphonic acid is obtained, known commercially as *Tropæolin Y;* with resorcinol the analogous *Chrysoïn* or *Tropæolin O* results; α-naphthol gives Poirrier's *Orange I,* or *Tropæolin OOO* No. 1; while β-naphthol yields Poirrier's *Orange II* or *Mandarin.*

In the case of the foregoing colours it is always the amine which is sulphonated. On the other hand, if the phenol be first sulphonated, and then caused to act on a diazotised chloride, substances are obtained which are isomeric with the former, but possess very different colouring and other properties. *Crocein Orange* is a dye of this class.

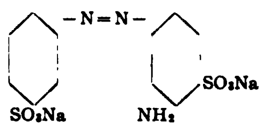
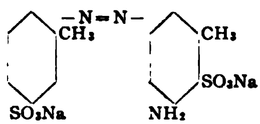
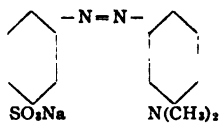
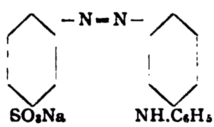
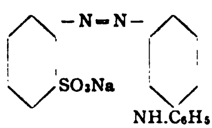
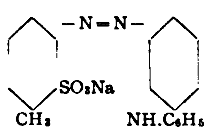
Tropæolins. Yellow and Orange Sulphonated Azo-dyes.

When diazobenzene-sulphonic acid acts on amines or alkaline solutions of phenols, a series of colouring matters are obtained, ranging from yellow to deep orange, and called Tropæolins. They usually occur in commerce as sodium salts, and are distinguished according to their shades, Tropæolin Y being the most yellow, and then O, OO, and so on, as the shade becomes redder.[2] The shade of colour becomes redder by the substitution of toluene, xylene, or cumene for benzene, and hence some of the higher homologues are considered in the section on "azo-reds."

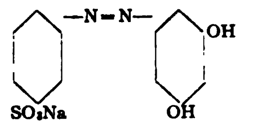
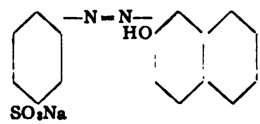
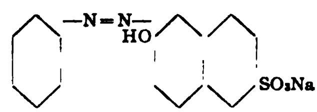
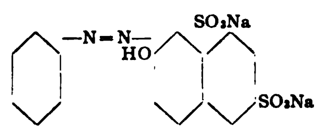
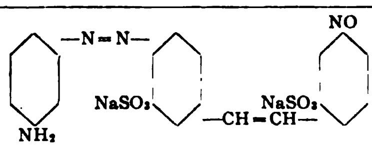
The following is a list of a few of the yellow and orange dyes of this class of commercial importance:

[1] See Vol. 6.

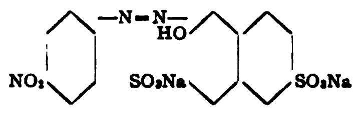
[2] A valuable paper by O. Mühlhäuser, on the manufacture of the orange azo-dyes, will be found in the *Dingl. Polyp. J.*, 1884, 4.

Commercial name	Chemical name or nature	Formula	Remarks
Amino-Azo-Dyes Acid Yellow. Fast Yellow. Acid Yellow G. Fast Yellow G. Fast Yellow extra. New Yellow L. Jaune Acide.	Mixture of sodium aminoazobenzene disulphonate with sodium amino-azo-benzene mono-sulphonate.		....
Fast Yellow R. Fast Yellow. Yellow W.	Sodium salt of aminoazotoluene disulphonic acid.		....
Helianthin. Methyl Orange Poirrier's Orange III. Dimethylaniline Orange. Tropæolin D.	Sodium salt of parasulphobenzene-azodimethylaniline.		....
Diphenylamine Orange. Orange IV. Tropæolin OO. Orange M. Fast Yellow. Orange GS. New Yellow. Ocange W. Acid Yellow D.[1]	K or Na salt of diphenyl-amine-azo-benzene-para-sulphonic acid.		....
Metanil Yellow.[2] Orange MN. Tropæolin G.	Na salt of diphenyl-amine-azo-benzene-meta-sulphonic acid,		....
Fast Yellow N. Curcumein. Yellow OO.	Na salt of di-phenylamine-azo-toluene-sulphonic acid.		Two isomers occur.

[1] *Brilliant yellow S* is the sodium sulphonate of Orange IV.
[2] The sulphonic acid of Metanil Yellow is known as *Metanil Yellow S.*

Commercial name	Chemical name or nature	Formula	Remarks
Amino-Azo-Dyes. Azoflavine. Azo Yellow. Azo Acid Yellow. Indian Yellow.[1]	A mixture of nitro-derivatives of diphenylamine.		
Hydroxy-Azo-Dyes. Tropæolin R or O.[2] Rescorcin Yellow. Chrysoin. Chryseolin. Yellow T. Gold Yellow. Acme Yellow.	Na salt of Resorcinol-*p*-sulphonic acid.		Seldom met with.
Tropæolin OOO No. 2.[3] Orange II. β-Naphthol Orange. Mandarin G. Chrysaurein. Gold Orange. Orange Extra. Atlas Orange.	Na salt of β-naphthol-azobenzene-*p*-sulphonic acid.		
Crocein Orange. Brilliant Orange. Orange GRx. Ponceau 4GB.[4]	Na salt of Benzene-azo-β-naphthol-sulphonic acid.		
Orange G. Orange Yellow Orange GG.[5]	Na salt of Benzene-azo-β-naphthol-disulphonic acid G.		Homologues are red.
Diphenyl Orange RR.	Na salt of nitroso-stilbene-disulphonic acid azoaniline.		Direct cotton dyestuff.

[1] By the action of nitric acid on diphenylamine yellow, *Curcumein* (*New Yellow*, *Citronin*) is first formed; then by further action Azo-acid Yellow.
[2] *Tropæolin Y*, the sodium salt of phenol-azo-benzene-p-sulphonic acid is obsolete.
[3] *Orange I*, *Tropæolin OOO No.* 1, *Sulphanaphthol Orange*, *Naphthol Orange* or *Orange B*, the corresponding dye from *a*-naphthol, is obsolete. *Orange R*, *Mandarin G R*, *Orange T*,

Commercial name	Chemical name or nature	Formula	Remarks
Hydroxy-Azo-Dyes. Orange No. 3 (not Helianthin).	Na salt of *m*-Nitrobenzene-azo-*β*-naphthol-disulphonic acid.		Not often met with.
Alizarin Yellow GG.	*m*-Nitrobenzene-azo-salicylic acid.	$C_6H_4\left\{\begin{matrix}(3)NO_2\\(1)N=N-(1)C_6H_3\left\{\begin{matrix}(4)OH\\(3)CO_2H\end{matrix}\right.\end{matrix}\right.$	Though requiring a mordant, is not a true alizarin.
Alizarin Yellow R.	*p*-Nitrobenzene-azo-salicylic acid.	$C_6H_4\left\{\begin{matrix}(4)NO_2\\(1)N=N-(1)C_6H_3\left\{\begin{matrix}(4)OH\\(3)CO_2H\end{matrix}\right.\end{matrix}\right.$	
Lancaster Yellow.	Dinitro-phenol-azo-phenol.	$C_6H_2\left\{\begin{matrix}(NO_2)_2\\OH\\N=N-C_6H_4.OH\end{matrix}\right.$	Obsolete.
Milling Yellow.	Sodium salt of sulphonaphthalene-azo-salicylic acid.	$C_{10}H_6\left\{\begin{matrix}SO_3Na\\N=N(4)C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2H\end{matrix}\right.\end{matrix}\right.$	Used with chrome mordant.
Yellow-fast-to-soap.	Sodium salt of meta-carboxy benzene-azodiphenylamine.	$C_6H_4\left\{\begin{matrix}(3)CO_2Na\\(1)N=N-(1)C_6H_4(4)NH.C_6H_5\end{matrix}\right.$	Dyed from a soap bath.
Oriol Yellow. Alkali Yellow. Cotton Yellow R.	Sodium salt of primuline-azo-salicylic acid.	$P-N=N-(4)C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right.$ (P = radical of primuline.)	
Persian Yellow.	Nitro-compound of *p*-toluene-azo-salicylic acid.	$C_6H_3\left\{\begin{matrix}CH_3\\N=N-C_6H_2\left\{\begin{matrix}OH\\CO_2H\\NO_2(?)\end{matrix}\right.\end{matrix}\right.$	
Narcein.	Sodium bisulphite compound of *p*-sulpho-benzene-azo-*β*-naphthol.	$C_6H_4\left\{\begin{matrix}(4)SO_3Na\\(1)NH—N(SO_3Na)—(1)C_{10}H_6(2)OH\end{matrix}\right.$	

or *Kermesin Orange* and *Orange 2 R*, are homologues of *Orange II*, being derived from toluidine and xylidine respectively, instead of from aniline.

[4] *Tropæolin OOOO*, the corresponding dye from *a*-naphthol, is obsolete. *Orange GT*, or *Orange RN* and *Scarlet GR* or *Scarlet R* are homologues prepared respectively from toluidine and xylidine instead of aniline.

[5] *Ponceau 2 G* is isomeric with Orange G, and *Ponceau G T* and *R T* are homologues from toluidine.

The following table shows the general character and reactions of the more important orange and yellow sulphonated azo-dyes:

Commercial name of dye	Character of solid dye of commerce	Colour of aqueous solution	Behaviour of aqueous solution with reagents				Reaction of solid dye with sulphuric acid		Products formed on reduction with zinc and hydrochloric acid
			On adding sodium hydroxide	On adding hydrochloric acid	With barium chloride	With calcium chloride	With strong acid	On dilution with water	
AMINO-AZO-DYES.									
Acid Yellow..	Yellow powder.	Yellow.	No change.	Yellow ppt. soluble in excess with reddish-yellow or cherry-red colour.	Precipitate.	No precipitate.	Brownish yellow.	Orange-yellow.	Sulphanilic acid and p-diaminobenzene.
Fast Yellow R.	Brownish-yellow powder.	Yellow.	No change.	Magenta-red.	....	....	Yellowish-brown.	Magenta-red	....
Helianthin; Methyl orange.	Orange-yellow powder.	Orange.	No change; orange ppt.	Red-violet; crystalline ppt. in strong solution.	....	....	Yellow or reddish-brown.	Carmine-red.	Sulphanilic acid and dimethyl-p-di-aminobenzene.
Diphenylamine Yellow.	Orange-yellow crystalline powder.	Yellow.	No change.	Red colour; or violet precipitate.	Precipitate.	Precipitate.	Violet.	Reddish-violet with slate-grey precipitate.	Sulphanilic acid and p-amino-di-phenylamine.
Metanil Yellow.	Brownish-yellow powder.	Orange.	No change.	Precipitate and crimson-red colour.	Sparingly soluble ppt.	Sparingly soluble ppt.	Dirty violet.	Magenta-red.	Aminobenzene-meta-sulphonic acid and p-amino-di-phenylamine.
Orange N.....	Orange-red, sparingly soluble.	Yellow.	Yellow ppt.	Violet or steel-blue ppt.	Yellow crystalline ppt.	....	Bluish-green.	Violet with steel-blue ppt.	....

Commercial name of dye	Character of solid dye of commerce	Colour of aqueous solution	Behaviour of aqueous solution with reagents: On adding sodium hydroxide	On adding hyhrochloric acid	With barium chloride	With calcium chloride	Reaction of solid dye with sulphuric acid: With conc. acid	On dilution with water	Products formed on reduction with zinc and hydrochloric acid
AMINO-AZO-DYES. Azoflavine....	Ochre-yellow powder.	Yellow.	Yellow-brown colour.	Reddish-violet or brownish.	Sparingly soluble crystalline ppt.	No precipitate.	Reddish-violet.	Red and brown yellow ppt.	....
HYDROXY-AZO-DYES. Tropæolin Y..	Brownish-yellow powder.	Reddish-yellow.	No change.	No change.	....	....	Brownish-yellow.	No change.	Sulphanilic acid and amino-phenol.
Resorcin Yellow; Chrysoin.	Brown powder.	Orange.	Reddish-brown.	No change.	....	....	Orange-yellow.	Reddish-yellow.	Sulphanilic acid and amino-resorcinol.
Orange I; α-Naphthol Yellow.	Brick-red powder.	Orange.	Red-brown.	Yellow-brown flakes.	....	Red precipitate.	Violet.	Brown precipitate; followed by orange solution.	Sulphanilic acid and amino-α naphthol.
Orange II; β-Naphthol Yellow; Mandarin.	Yellow-red powder.	Orange.	Changed to brown-red.	Brownish-yellow ppt. in strong solutions only.	Sparingly soluble crystalline precipitate.	Yellow ppt., becoming dirty red and crystalline on boiling with water.	Carmine-red.	Brownish-yellow precipitate.	Sulphanilic acid and amino-β-naphthol.
Crocein Orange.	....	....	....	Yellow-brown precipitate.	....	....	Orange-yellow.	Yellow-brown precipitate.	Aniline, amino-β-naphthol sulphonic acid.
Orange G.....	Yellowish-red powder.	Reddish-yellow.	Changed to brown.	Not changed.	....	Orange scales.	Orange-yellow.	Unchanged.	Aniline, amino β-naphthol sulphonic acid.

Commercial name of dye	Character of solid dye of commerce	Colour of aqueous solution	Behaviour of aqueous solution with reagents				Reaction of solid dye with sulphuric acid		Products formed on reduction with zinc and hydrochloric acid
			On adding sodium hydroxide	On adding hydrochloric acid	With barium chloride	With calcium chloride	With conc. acid	On dilution with water	
HYDROXY-AZO-DYES. Orange No. 3 (not Helianthin).	Red-brown powder.	Reddish-yellow.	Changed to yellowish-brown.	Orange-yellow precipitate, soluble in much water.	....	....	Orange-yellow.	Orange ppt.; soluble in excess of water to a yellow solution.	Nitraniline, amino-β-naphthol, sulphonic acid.
Alizarin yellow G. G.	Yellow paste or powder.	Yellow.	Orange yellow solution.	Yellow ppt.	Unchanged.	Unchanged.	Orange-yellow.	Yellow ppt.	....
Alizarin yellow R.	Brown paste.	Orange.	Blood-red solution.	Yellow ppt.	Yellow-brown residue.	Yellow-brown residue.	Orange-red.	Brown ppt.	....
Lancaster Yellow.	Dark-brown crystals.	Brownish-yellow.	Yellow-red.	....	....	....	Reddish-yellow.	....	....
Milling Yellow.	Yellow powder.	Yellow.	Orange.	Brown ppt.	....	....	Yellowish-red.	....	....
Yellow-fast-to-soap.	Brown paste.	Yellow-brown.	No change.	Reddish-violet.	....	....	Violet.	Ruby-red.	....
Clayton Yellow.	Yellow powder.	Yellow.	Orange ppt.	Orange ppt.	....	....	Brownish-yellow.	Paler.	....
Oriol Yellow..	Red powder.	Orange.	Redder.	Yellow ppt.	....	....	Scarlet.	Yellow ppt.	....
Persian Yellow.	Brownish-yellow powder.	Yellow.	Orange.	Brown ppt.	....	....	Orange.	Brown ppt.	....
Narcein......	Orange powder.	Yellow.	Brownish-red.	No change.	....	....	Yellowish-brown.	Evolves SO_2 when warmed.	....

The best way of effecting the reduction of the yellow or orange azo-dyes is to warm the solution of the colouring matter with zinc-dust and hydrochloric acid, the action in an ammoniacal solution being somewhat slow. Reduction with ammonium sulphide may sometimes be conveniently employed.

The following is a detailed description of some of the more important sulphonated azo-yellows and oranges:

Acid Yellow. Fast Yellow.[1] — Amino-azobenzene-sulphonic acid, $C_6H_4(SO_3H).N_2.C_6H_4(NH_2)$, is a yellow powder and forms the *Solid Yellow S* of commerce.[2] The commercial product known as *Acid Yellow* is prepared by dissolving the sulphonic acid in sodium carbonate and precipitating the solution by common salt. Acid Yellow is a yellow powder, readily forming a yellow solution in water, but only sparingly soluble in alcohol. On acidifying the aqueous solution with hydrochloric acid the free sulphonic acid is thrown down in the form of minute needles, soluble in excess of hydrochloric acid with reddish-yellow colour, appearing crimson in thin layers, the change being probably due to the formation of a hydrochloride. Acid Yellow is not precipitated by ammonia, fixed alkalies, or basic lead acetate. It is precipitated by barium chloride, but not by calcium chloride. Sulphuric acid dissolves the solid dye with a yellow colour. Zinc-dust decolourises the solution, but the filtered liquid recovers its yellow colour on exposure to the air.

Acid Yellow is used for dyeing wool and silk, but it is not often used alone for pure yellow colours; for although it is comparatively fast and will stand steaming, it is not sufficiently bright, and is sensitive to acids. As its shade is fairly pure it is adapted for use in compound colours, such as olive- and moss-green, and browns, where it replaces the natural yellow dyestuffs, it being as fast to light as the best of the latter. Acid Yellow is also used extensively for the manufacture of diazo-colours.

Fast Yellow R is produced in a manner analogous to Acid Yellow, by sulphonating aminoazotoluene. It is a brownish-yellow powder, giving a yellow solution with water. Its application is similar to Acid Yellow, but its shade is orange-yellow.

Methyl Orange. Helianthin. Tropæolin D. Orange III. Gold

[1] *Acid Yellow G* (gelb) is a derivative of amino-azobenzene. The homologue from amino-azotoluene is somewhat more orange in shade, and is known as *Acid Yellow R*, or *Fast Yellow R*. The name *Fast Yellow* is also applied to diphenylamine yellow and to a substance of the formula, $C_6H_4(COOH).N_2.C_6H_4.NH(C_6H_5)$.

[2] Much of the Acid Yellow of commerce contains more or less of a disulphonate.

Orange. Mandarin Orange. These names, among others, are applied to the ammonium or sodium salt of *p*-dimethyl-amino-azo-benzene-sulphonic acid, $C_6H_4(SO_3H)(4).N_2(1).C_6H_4.N(CH_3)_2(4)$. Helianthin forms an orange-yellow powder, readily soluble in hot water, but only sparingly so in alcohol. The aqueous solution is orange-yellow, and is not precipitated by alkalies. On adding excess of hydrochloric acid to a hot, concentrated aqueous solution, the free sulphonic acid is precipitated in microscopic needles, which soon change to small, strongly lustrous plates or prisms showing a violet reflection. Concentrated sulphuric acid dissolves helianthin with reddish or yellowish-brown colour, the solution appearing yellow in thin layers. On further dilution, the liquid assumes a splendid red colour. With most reagents, helianthin behaves similarly to Acid Yellow, but basic acetate of lead throws down the whole of the colouring matter as an orange-yellow precipitate. Sodium chloride or magnesium sulphate added to a dilute solution of helianthin precipitate a colouring matter in microscopic crystals.

Silk and wool when immersed in an acid solution of helianthin are dyed a fiery orange. The dyed fibre is turned red by hydrochloric acid and yellow by strong sulphuric acid, but alkalies produce no change.

Methyl-orange is in general use as an indicator in alkalimetry.

Diphenylamine Yellow.—This colouring matter, also known as *Tropæolin OO*, and *Orange MN*, *Gold-Orange*, *Acid-Yellow D*, *Diphenylamine-Orange*, *Fast-Yellow*, and *Manchester-Yellow*, is a phenylated Acid Yellow. The free acid forms steel-grey needles, very sparingly soluble in water with pink colouration. It is a powerful acid, forming well-defined salts, almost all of which are remarkable for their insolubility. The commercial dye is a potassium or sodium salt and forms an orange-yellow crystalline powder or golden-yellow dichroïc crystals. It is readily soluble in hot water, but only very sparingly so in cold water or alcohol. Very small quantities of mineral salts precipitate it from its solutions. The hot aqueous solution is yellow and unchanged by alkali hydroxides, but is turned reddish-violet by hydrochloric acid, and on cooling a violet precipitate is formed. Calcium and barium chlorides give yellow crystalline precipitates. In strong sulphuric acid the dye dissolves with violet colour, becoming redder on adding water, while a slate-grey precipitate is produced.

When reduced with an acid solution of stannous chloride, Tropæolin

OO yields sulphanilic acid and *p*-amino-diphenylamine, which may be extracted by ether after adding excess of sodium hydroxide to the solution.

Diphenylamine yellow gives a fine golden-yellow on silk or wool. The fibre is turned blue-violet by sulphuric and red-violet by hydrochloric acid.

Tropæolin OO may be substituted for methyl-orange as an indicator in alkalimetry, a faint trace of strong mineral acid turning the dilute solution red, while carbonic and other weak acids have no effect.

Metanil yellow is isomeric with diphenylamine yellow. *Brilliant Yellow*, *Acid Yellow OO*, *Yellow N*, and *Orange N* are names given to the homologues of diphenylamine yellow.

Orange II from β-naphthol and diazotised sulphanilic acid is not sensitive to either acids or alkalies, and is extensively employed in wool-dyeing, both as a self-colour and in compound shades.

Azoflavine is a mixture of mono-, di-, and tri-nitrodiphenylamine with the compound $C_6H_4(SO_3H).N_2.C_6H_4.NH(C_6H_4NO_2)$. It forms an ochre-yellow powder, soluble with difficulty in cold, but readily in hot water. The aqueous solution is yellow, changing to brownish on addition of hydrochloric acid. Barium chloride gives a slightly soluble crystalline precipitate, but no change results with calcium chloride. The solid dye dissolves in strong sulphuric acid with magenta-red colour, changing to yellowish-red, with a yellowish-brown precipitate, on dilution with water. When heated on platinum foil the dye forms "Pharaoh's serpents," and gives off yellow vapours.

Azoflavine S or 2, *Azo-Yellow*, *Citronine B* or 2 *B*, *Indian Yellow*, and *New Yellow*, are names which have been applied to varieties of Azoflavine.

Azo-reds.

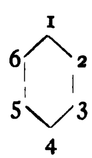
The scarlets, ponceaus, and clarets derived from azobenzene and its allies are among the most important of the colouring matters from coal-tar.

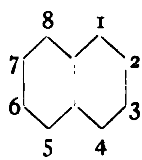
The following table contains a description of some of the more important azo-dyes of which xylidine-scarlet is the type. The commercial names of the dyes are often confusing, the same chemical compound receiving different names from its several makers, while, on the

other hand, identical or very similar names are commercially used to distinguish dyes of distinctly different chemical nature.

Owing to the facility with which diazo-compounds react with phenols and their sulphonic acids in alkaline solution, it is possible to produce azo-dyes directly on the fibre by immersing the goods alternately or simultaneously in a solution of naphthol and the diazo salt, and then developing the colour in an alkaline bath. The method is especially applicable to cotton. The colouring matter known as *Primuline* can be diazotised in the fabric, and on subsequently immersing the goods in an alkaline solution of resorcinol or naphthol the azo-dye is developed. Another method of utilising this diazo-reaction is to develop on the fibre a diazo colour by coupling it with diazotised paranitraniline in an alkaline bath. Primuline, the diamine nitrazole colours, and some other derivatives of benzidine are capable of undergoing this so-called "coupling process." The peculiarity of this method is that the developer and not the dyestuff is diazotised. The property possessed by the hydroxy-azo-dyes of forming soluble compounds with sodium hydrogen sulphite which are decomposed by heat is also utilised. *Narceine*, $C_6H_4(SO_3Na).NH.N(NaSO_3).C_{10}H_6.OH\beta$, is a substance of this class. It is a compound of Orange II with sodium hydrogen sulphite, and has been used in calico-printing. It is decomposed on steaming, sulphurous acid being liberated and Orange II reformed.

The letters appended to the commercial names of dyestuffs are usually indicative of the particular shade, R. referring to red, G to yellow (gelb), and B to blue; 2R, etc., means a deeper shade of red than a single R. At times other letters are employed for the purpose of trade distinctions, and refer to some private nomenclature of the manufacturing firm. The formulæ indicate as far as possible the structure of the molecule and the relative positions of the substituting groups in the benzene and naphthalene nuclei; the large figures in brackets placed before the different substituting groups refer to these positions in the nuclei, as shown by the following diagrams:



for benzene, and


for naphthalene.

Commercial name	Formula	Remarks	Character of dye
Archil substitute. Naphthionic Red.	$C_6H_4\left\{\begin{matrix}(4)NO_2\\(1)N=N(2)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$	From naphthionic acid.	Brown paste; red-brown solution.
Cochineal Scarlet 2 R.	$C_6H_4(CH_3)-N=N-C_{10}H_5\left\{\begin{matrix}(1)OH\\(5)SO_3Na\end{matrix}\right.$	From C acid. Homologue is scarlet 4 R.	Cinnabar-red powder, soluble in hot water to yellow-red solution.
Scarlet G T.	$C_6H_4(CH_3)-N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)OH\\(6)SO_3Na\end{matrix}\right.$	From S acid. Homologue is scarlet G R.	Scarlet powder; solution orange-yellow.
Azococcin 2 R.	$C_6H_3(CH_3)_2-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$	From Neville's acid.	Brown-red powder, difficultly soluble; bronzy crystals on cooling.
Wool Scarlet R.	$C_6H_3(CH_3)_2-N=N-(1)C_{10}H_4\left\{\begin{matrix}(1)OH\\(4)SO_3Na\\(8)SO_3Na\end{matrix}\right.$	From R salt. Schoellkropf acid.	Brown-red powder; solution yellowish-red.
Ponceau 2 R. Scarlet R. Xylidine Scarlet	$C_6H_3(CH_3)_2-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.$	From R salt. Isomers of yellower shade from G salt. Ponceau G, and Scarlet G.	Scarlet powder; easily soluble; red solution.
Ponceau 2 G. Scarlet 2 G and 2 R.	$C_6H_5-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.$	From G salt. Isomers from R salt.	Brown-red powder. Fine red solution.
Ponceau 3 R.[1]	$C_6H_2\left\{\begin{matrix}(5)CH_3\\(4)CH_3\\(2)CH_3\\(1)N=N-C_{10}H_4\left\{\begin{matrix}OH\beta\\(SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$	From R salt.	Dark red powder; solution cherry-red.
Anisol Red. Anisidine Ponceau.	$C_6H_4\left\{\begin{matrix}(1)OCH_3\\(2)N=N-(1)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(2)OH\\(6)SO_3Na\end{matrix}\right.$	From R salt.	Brownish-red powder; solution cherry-red.
Phenetol Red. Coccinin. Coccin.	$C_6H_4\left\{\begin{matrix}(2)OC_2H_5\\(1)N=N-C_{10}H_4\left\{\begin{matrix}OH\beta\\(SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$	From R salt.	Fine red solution.
Coccinin B.	$C_6H_3\left\{\begin{matrix}(1)CH_3\\(4)OCH_3\\(3)N=N-C_{10}H_4\left\{\begin{matrix}OH\beta\\(SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$	From R salt.	Dark red powder; solution cherry-red.
Crystal Ponceau 6 R.	$C_{10}H_7(1)-N=N(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{matrix}\right.$	From G acid.	Red-brown, glittering crystals; solution deep red.
Fast Brown N; Azo Brown O; Napthylamine Brown; Chrome Brown R O.	$C_{10}H_6\left\{\begin{matrix}(4)SO_3Na\\(1)N=N-(4)C_{10}H_6(1)OH\end{matrix}\right.$	From naphthionic acid.	Dark brown powder; solution yellowish-brown.

1 There is also a *Ponceau* 3 *R* which is the sodium salt of ethyldimethyl-benzene-azo-β-naphthol-disulphonic acid.

Reaction of aqueous solution		Reaction of dye with sulphuric acid		Products of reduction with zinc and ammonia	Other characters
With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water		
Precipitate soluble in water.	Precipitate.	Magenta-red.	Brown-red ppt.	Nitraniline and diamino-naphthalene sulphonic acid.	
Orange colouration.	Red flakes.	Magenta-red.	Red flakes.	Toluidine and amino-α-naphthol sulphonic acid.	
Brown-red colouration.	Brown oily drops.	Magenta-red.	Oily drops.	Toluidine and amino-β-naphthol sulphonic acid.	
Brown-yellow-colour; no ppt.	Brownish-red flakes.	Magenta-red.	Brown-red precipitate.	Xylidine and amino-α-naphtholsulphonic acid.	
Yellow-red colour.	Bluish-red colouration.	Cherry-red.	Red solution.	Xylidine and amino-α-naphtholdisulphonic acid.	
No precipitate.	No change.	Red.	Brown precipitate.	Amino-β-naphtholdisulphonic acid and xylidine.	$BaCl_2$ and $CaCl_2$, amorphous precipitates.
No change.	No change.	Eosin-red.	Yellow-red colour.	Amino-β-naphtholdisulphonic acid and cumidine.	$BaCl_2$ and $CaCl_2$ precipitates appearing slowly.
Yellow precipitate.	No change.	Cherry-red.	Cherry-red.	Amino-β-naphtholdisulphonic acid and ethyl-xylidine.	
Yellowish-red.	No change.	Magenta-red.	Cherry-red.	Amino-β-naphtholdisulphonic acid and anisidine.	
Brownish colouration.	....	Magenta-red.	Red.	Amino-β-naphtholdisulphonic acid and phenatidine.	$BaCl_2$, brown, sparingly soluble precipitate. $CaCl_2$ red precipitate gradually.
Brown ppt. soluble to red-brown solution.	Darkened.	Magenta- or cherry-red.	Cherry-red.	Amino-β-naphtholdisulphonic acid and methyl anisidine.	$BaCl_2$, brown ppt. $CaCl_2$, red precipitate formed gradually.
Bright brown.	Darkened; with excess, brown crystalline ppt.	Violet.	Scarlet.		
Reddish-brown.	Magenta-red.	Violet solution.	Magneta red.	Amino-α-naphthol and 1:4 amino-naphtholsulphonic acid.	Dyes wool brown from an acid bath.

Commercial name	Formula	Remarks	Character of dye
Roccelline. Fast Red A. Rubidine. Cerasine.	$C_{10}H_6\left\{\begin{matrix}(4)SO_3Na\\(1)N=N-(1)C_{10}H_6(2)OH\end{matrix}\right.$	From naphthionic acid.	Solution reddish-brown, forms brown jelly when rapidly cooled.
Fast Red C. Azorubin S. Carmoisin.	$C_{10}H_6\left\{\begin{matrix}(4)SO_3Na\\(1)N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From naphthionic acid and Neville's acid.	Brown powder; magenta-red solution.
New Coccin. Brilliant Ponceau.	$C_{10}H_6\left\{\begin{matrix}(4)SO_3Na\\(1)N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From naphthionic acid and G salt.	Scarlet-red powder; sparingly soluble.
Fast Red D. Amaranth.	$C_{10}H_6\left\{\begin{matrix}(4)SO_3Na\\(1)N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From naphthionic acid and R salt.	Reddish-brown powder; solution magenta-red.
Cochineal. Scarlet G.	$C_6H_5-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)OH\\(5)SO_3Na\end{matrix}\right.$	From L acid.	Brick-red powder; yellow solution.
Brown N P and N P J.	$C_6H_4\left\{\begin{matrix}(4)NO_2\\(1)N=N-(1)C_6H_2\left\{\begin{matrix}(2)OH\\(3)OH\\(4)OH\end{matrix}\right.\end{matrix}\right.$	From diazotized *p*-nitraniline and pyrogallol.	Brown paste.
Archil Substitute G.	$C_6H_4\left\{\begin{matrix}(4)NO_2\\(1)N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)NH_2\\(6)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From *p*-nitraniline and *β*-naphthylamine.	Brown powder; red solution.
Archil Substitute 3 VN.	$C_6H_4\left\{\begin{matrix}(4)NO_2\\(1)N=N-C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(5)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From L acid.	Brown powder; red solution.
Archil Substitute Extra. Apollo Red.	$C_6H_4\left\{\begin{matrix}(4)NO_2\\(1)N=N-C_{10}H_4\left\{\begin{matrix}NH_2\\(SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$	From *p*-nitraniline and *α*-naphthylamine-disulphonic acid.	Brown powder; red solution.
Ponceau R T.	$C_6H_4\left\{\begin{matrix}CH_3\\N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From R acid.	Red powder; orange solution.
Cochineal. Scarlet 4 R.	$C_6H_3(CH_3)_2-N=N-C_{10}H_5\left\{\begin{matrix}(1)OH\\(5)SO_3Na\end{matrix}\right.$	From L acid.	Red powder; slightly soluble.
Scarlet G R. Scarlet R.	$C_6H_3(CH_3)_2-N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)OH\\(6)SO_3Na\end{matrix}\right.$	From S acid.	Red powder; orange solution.
Palatine. Scarlet.	$C_6H_3(CH_3)_2-N=N-C_{10}H_4\left\{\begin{matrix}OH\\(SO_3Na)_2\end{matrix}\right.$	From naphthol-disulphonic acid.	Red powder; red solution.
Ponceau G. Scarlet G.	$C_6H_3(CH_3)_2—N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{matrix}\right.$	From G acid.	Red powder; red solution.
Ponceau 3 R.	$C_6H_2\left\{\begin{matrix}C_2H_5\\(CH_3)_2\\N=N-C_{10}H_4\left\{\begin{matrix}OH\beta\\(SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$	....	Red powder; red solution.
Azo-eosin.	$C_6H_3\left\{\begin{matrix}(2)OCH_3\\(1)N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.\end{matrix}\right.$	From N W acid.	Red powder; red solution.

Reaction of aqueous solution		Reaction of dye with sulphuric acid		Products of reduction with zinc and ammonia	Other characters
With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water		
Darkened.	Yellow-brown ppt.	Violet.	Yellow-brown ppt.	Naphthionic acid, and amino-β-naphthol.	Na_2CO_3 in strong solution gives pale brown crystals.
Becomes yellow.	Brown jelly.	Bluish-violet.	Magenta-red.	α-naphthylaminesulphonic acid and amino-α-naphthol sulphonic acid.	$CaCl_2$, red crystalline precipitate.
Brown.	No change.	Magenta-red.	Yellow-red.	α-naphthylaminesulphonic acid and amino-β-naphtholdisulphonic acid.	
Becomes dark.	No change.	Violet.	Magenta-red.		
Orange.	Thick ppt.	Cherry-red.	Red ppt.		
Brown ppt.	Brown ppt.	Red.	Brown ppt.		
Brown.	Bluish ppt.	Red.	No change.		
Brown ppt.	Crimson.	Crimson.	No change.		
Yellow.	No change.	Red.	Orange.		
Yellowish-Red.	Brown ppt.	Magenta-red.	Red ppt.		
No change.	Brown ppt.	Red.	Red ppt.		
Yellower.	Brown ppt.	Purple.	Brown ppt.	....	Soluble in alcohol.
No change.	No change.	Red.	Orange.		
Yellow ppt.	No change.	Red.	No change.		
Yellowish.	Brown ppt.	Red.	Red ppt.	....	Slightly soluble in alcohol.

Commercial name	Formula	Remarks
Orcellin Deep Red.	$C_6H_2\left\{\begin{array}{l}OH\\(NO_2)_2\\N=N-C_6H_3(OH)_2\end{array}\right.$	From Picramic acid and Resorcinol.
Fast Red B T.	$C_{10}H_7(1)N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(6)SO_3Na\end{array}\right.$	From S acid.
Fast Red B. Bordeaux B.	$C_{10}H_7(1)N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.$	From R acid.
Palatine Red.	$C_{10}H_7(1)N=N-C_{10}H_4\left\{\begin{array}{l}OH\\(SO_3Na)_2\end{array}\right.$	....
Crocein 3 B X.	$C_{10}H_6\left\{\begin{array}{l}(4)SO_3Na\\(1)N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(8)SO_3Na\end{array}\right.\end{array}\right.$	From B acid.
Fast Red E. Fast Red.	$C_{10}H_6\left\{\begin{array}{l}(4)SO_3Na\\(1)N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From S acid.
Scarlet 6 R. Ponceau 6 R.	$C_{10}H_6\left\{\begin{array}{l}(4)SO_3Na\\(1)N=N-C_{10}H_3\left\{\begin{array}{l}OH\beta\\(SO_3Na)_2\end{array}\right.\end{array}\right.$	From trisulphonic acid.
Acid Ponceau.	$C_{10}H_6\left\{\begin{array}{l}SO_3Na\\N=N-(1)C_{10}H_6(2)OH\end{array}\right.$	From α and γ naphthylamines.
Fast Brown 3 B.	$C_6H_4\left\{\begin{array}{l}(6)SO_3Na\\(2)N=N-(4)C_{10}H_6(1)OH\end{array}\right.$	....
Orange Red I. Double Brilliant Scarlet G.	$C_{10}H_6\left\{\begin{array}{l}(6)SO_3Na\\(2)N=N-(1)C_{10}H_6(2)OH\end{array}\right.$	....
Brilliant Ponceau 4 R. Double Scarlet Extra S. Double Brilliant Scarlet 3 R.	$C_{10}H_6\left\{\begin{array}{l}(6)SO_3Na\\(2)N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Pyrotine R R O.	$C_{10}H_6\left\{\begin{array}{l}(5)SO_3Na\\(2)N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Alkali Brown.	$P-N=N-(1)C_6H_3\left\{\begin{array}{l}(2)NH_2\\(4)NH_2\end{array}\right.$ (P = primuline radical.)	....
Atlas Red.	$P-N=N-(1)C_6H_2\left\{\begin{array}{l}(3)CH_3\\(4)NH_2\\(6)NH_2\end{array}\right.$	....

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown paste; red solution.	No change.	Brown pp.	Brown.	Brown pp.	Soluble in alcohol.
Red powder; red solution.	Brown.	Brown pp.	Violet.	Violet pp.	Slightly soluble in alcohol.
Brown powder; purple solution.	Yellow.	No change.	Blue.	Violet.	....
Blue powder; purple solution.	Yellower.	Brown pp.	Blue.	Brown pp.	....
Red powder; orange solution.	Brown.	No change.	Violet.	Orange.	....
Brown powder; red solution.	Brown.	No change.	Violet.	Red.	....
Brown powder; purple solution.	Brown.	No change.	Violet.	Magenta-red.	....
Red powder; slightly soluble.	Browner.	Brown pp.	Violet.	Brown pp.	Soluble in hot water.
Brown powder; brown solution.	Red.	Violet.	Blue.	Violet pp.	....
Brown powder; red solution.	Brown pp.	Brown pp.	Bluish-red.	Red pp.	....
Brown powder; orange solution.	No change.	Brown pp.	Bluish-red.	Scarlet.	....
Brown powder; orange solution.	Yellower.	Bluer.	Bluish-red.	Red.	....
Brown powder; red solution.	Red pp.	Brown pp.	Violet.	Brown pp.	Soluble in alcohol.
Red powder; brown solution.	....	Dark pp.	....	....	Gives brown shades when diazotised on fibre.

Commercial name	Formula	Remarks
Terra Cotta R.	$C_6H_5-N=N-C_6H_2\begin{cases}OH\\CO_2H\\NO_2\end{cases}$	....
Azo-fuchsin B.	$C_6H_4\begin{cases}CH_3\\N=N-C_{10}H_4\end{cases}\begin{cases}(1)OH\\(8)OH\\(4)SO_3Na\end{cases}$	From Schoellkopf's acid.
Azo-fuchsin G.	$C_6H_4\begin{cases}(4)SO_3Na\\(1)N=N-C_{10}H_4\end{cases}\begin{cases}(1)OH\\(8)OH\\(4)SO_3Na\end{cases}$	From Schoelkopf's acid.
Diamond Yellow G.	$C_6H_4\begin{cases}(3)CO_2Na\\(1)N=N-(4)C_6H_3\end{cases}\begin{cases}(1)OH\\(2)CO_2Na\end{cases}$	....
Diamond Yellow R.	$C_6H_4\begin{cases}(2)CO_2Na\\(1)N=N-(4)C_6H_3\end{cases}\begin{cases}(1)OH\\(2)CO_2Na\end{cases}$	....
Roxamin.	$C_{10}H_6\begin{cases}(4)SO_3Na\\(1)N=N-(1)C_{10}H_5\end{cases}\begin{cases}(2)OH\\(7)OH\end{cases}$	....
Chromotrope 2 R.	$C_6H_5N=N(2)C_{10}H_3\begin{cases}(1)OH\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}$	From chromotrope acid.
Chromotrope 2 B.	$C_6H_4\begin{cases}NO_2\\N=N(2)C_{10}H_3\end{cases}\begin{cases}(1)OH\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}$	From *p*-nitraniline and chromotrope acid.
Chromotrope 10 B.	$C_{10}H_7(a)N=N(2)C_{10}H_3\begin{cases}(1)OH\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}$	From chromotrope acid.
Chromotrope 8 B.	$C_{10}H_6\begin{cases}SO_3Na\\N=N(2)C_{10}H_3\end{cases}\begin{cases}(1)OH\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}$	From chromotrope and naphthionic acid.
Prager Alizarin Yellow G.	$C_6H_4\begin{cases}(4)NO_2\\(2)N=N-(2)C_6H_2\end{cases}\begin{cases}(3)OH\\(5)OH\\(6)CO_2Na\end{cases}$	From β-resorcyl acid and metanitraniline.
Prager Alizarin Yellow R.	$C_6H_4\begin{cases}(5)NO_2\\(2)N=N-(2)C_6H_2\end{cases}\begin{cases}(3)OH\\(5)OH\\(6)CO_2Na\end{cases}$	From β-resorcyl acid and paranitraniline.
Para-Nitraniline Red.	$C_6H_4\begin{cases}(4)NO_2\\(1)N=N-(1)C_{10}H_6(2)OH\end{cases}$	From para-nitraniline and β-naphthol.
Wool Violet S.	$C_6H_3\begin{cases}(1)NO_2\\(5)NO_2\\(2)N=N-(2)C_6H_3\end{cases}\begin{cases}(1)SO_3Na\\(5)N(C_2H_5)_2\end{cases}$	From dinitraniline.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics.
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; brown solution.	Red.	Brown pp.	Yellow.	Brown pp.	The presence of the NO_2 group is questioned.
Dark brown powder; red solution.	Bluer.	Brown pp.	Violet.	Bluish-red.	....
Brown powder; red solution.	Bluer.	Yellower.	Violet.	Bluish-red.	....
Yellow paste; yellow solution.	....	....	Orange.	Yellow pp.	More readily soluble in water containing sodium carbonate or acetate.
Brown paste; yellow solution.	....	....	Orange.	Yellow pp.	More readily soluble in water containing sodium carbonate or acetate.
Red powder; scarlet solution.	Darker.	No change.	Violet.	....	Acid dye for wool.
Red powder, magenta-red solution.	No change.	No change.	Violet.	Orange.	Soluble in alcohol. Acid dye for wool.
Red powder; orange solution.	Violet.	Yellower.	Violet.	Orange.	Soluble in alcohol. Acid and chrome dye for wool.
Violet powder; violet solution.	Orange.	No change.	Blue.	Violet pp.	Soluble in alcohol. Acid dye for wool.
Violet powder; violet solution.	No change.	No change.	Blue.	Violet.	Soluble in alcohol. Acid dye for wool.
Yellow powder; yellow solution.	Orange.	Yellow pp.	Yellow.	Yellow pp.	Soluble in alcohol. Chrome dye for wool.
Orange powder; orange solution.	Violet.	Orange ppt.	Orange.	Orange ppt.	Soluble in alcohol. Chrome dye for wool.
The dyestuff is made on the fibre.	....	....	....	....	Ingrain dye for cotton.
Black powder; violet solution.	Violet ppt.	Orange.	Scarlet.	Orange ppt.	Soluble in alcohol. Acid dye for wool.

Commercial name	Formula	Remarks
Victoria Violet 4 B S.	$C_6H_4\left\{\begin{matrix}NH_2\\ N{=}N-(2)C_{10}H_2\end{matrix}\right.\left\{\begin{matrix}(1)OH\\ (8)OH\\ (3)SO_3Na\\ (6)SO_3Na\end{matrix}\right.$	From Chromotrope 2 B.
Chromotrope 6 B.	$C_6H_4\left\{\begin{matrix}NH.C_2H_3O\\ N{=}N-(2)C_{10}H_2\end{matrix}\right.\left\{\begin{matrix}(1)OH\\ (8)OH\\ (3)SO_3Na\\ (6)SO_3Na\end{matrix}\right.$	From Chromotrope acid.
Spirit Yellow R. Yellow Fat Colour.	$C_6H_4\left\{\begin{matrix}(1)CH_3\\ (2)N{=}N-(2)C_6H_3\end{matrix}\right.\left\{\begin{matrix}(6)CH_3\\ (5)NH_2\end{matrix}\right.$	From ortho-toluidine.
Chrysoidin. R.	$C_6H_4\left\{\begin{matrix}(1)CH_3\\ (2)N{=}N-(2)C_6H_2\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\ (4)CH_3\\ (5)NH_2.HCl\end{matrix}\right.$	From ortho-toluidine.
Rose de Benzoyl.	$C_{10}H_5\left\{\begin{matrix}(1)OH\\ (4)SO_3Na\\ (2)N{=}N-C_{12}H_6\end{matrix}\right.\left\{\begin{matrix}NH.CO.C_6H_5\\ (CH_3)_2\end{matrix}\right.$	From N W acid.
Sulphamine Brown A. Naphthine Brown α.	Not determined.	From α-diazonaphthalene.
Azo Turkey Red.	$C_{10}H_7(3)N{=}N(1)C_{10}H_6(2)OH$	Developed on fibre from β-naphthylamine and β-naphthol.
Sulphamine Brown B. Naphthine Brown β.	Not determined.	From β-diazonaphthaline.
Diamond Flavin G.	$C_6H_3\left\{\begin{matrix}(3)CO_2H\\ (4)OH\\ (1)N{=}N-(1)C_6H_4.C_6H_4.(4)OH\end{matrix}\right.$	From salicylic acid.
Indoïn Blue R.	Not determined.	From safranine.
Phenoflavin	$C_6H_4\left\{\begin{matrix}(4)SO_3Na\\ (2)N{=}N(2)C_6H_2\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\ (3)SO_3Na\\ (5)OH\end{matrix}\right.$	From metanilic acid.
Fast Red B.	$C_{10}H_6\left\{\begin{matrix}SO_3Na\\ N{=}N-C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}OH\\ CH_2.C_{10}H_6.OH\end{matrix}\right.$	From naphthionic acid.
Fast Acid Scarlet. Fast Acid Ponceau.	$C_{10}H_6\left\{\begin{matrix}(4)SO_3Na\\ (6)N{=}N-(1)C_{10}H_6.(2)OH\end{matrix}\right.$	From beta-acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Green powder; violet solution.	Orange.	Orange.	Violet.	Orange ppt.	Soluble in alcohol. Acid dye for wool.
Brown powder; violet solution.	Yellow.	No change.	Red.	Violet ppt.	Soluble in alcohol. Acid dye for wool.
Yellow lumps; but slightly soluble, melt in boiling water.	....	Red crystals	Brown.	Red ppt.	Soluble in hot alcohol. Colour for fats, butter, etc.
Violet crystals; red solution.	Yellow ppt.	Brown ppt.	Brown.	Red ppt.	Soluble in alcohol.
Red lumps.	Red.	Violet ppt.	Red.	....	Direct dye for cotton.
Brown powder; brown solution.	Brown ppt.	No change.	Green.	Brown.	Chrome dye for wool.
....	....	....	....	....	Ingrain colour.
Brown powder; brown solution.	Brown ppt.	No change.	Violet.	Brown.	Chrome dye for wool.
Brown paste; insoluble.	Orange solution.	No change.	Red.	Brown ppt.	Soluble in alcohol.
Brown paste or powder; violet solution.	Violet ppt.	Blue ppt.	Green.	Violet ppt.	Soluble in alcohol. Direct colour for cotton.
Yellow powder; yellow solution.	Orange.	Orange.	Yellow.	....	Acid dye for wool.
Brown powder; red solution.	Darker.	Brown ppt.	Violet.	Brown ppt.	Acid dye for wool.
Red powder; but slightly soluble.	Darker.	Brown pp.	Violet.	Brown pp.	Acid dye for wool.

Commercial name	Formula	Remarks
Chrome Yellow D. Anthracene Yellow B N. Milling Yellow.	$C_{10}H_6\begin{cases}(6)SO_3Na\\(2)N=N-(2)C_6H_3\begin{cases}(4)CO_2H\\(5)OH\end{cases}\end{cases}$	From salicylic acid.
Crumpsall-Yellow.	$C_{10}H_5\begin{cases}(6)SO_3Na\\(8)SO_3Na\\(2)N=N-(2)C_6H_3\begin{cases}(4)CO_2H\\(5)OH\end{cases}\end{cases}$	From salicylic acid.
Cotton Orange G.	$P-N=N(2)C_6H\begin{cases}(1)NH_2\\(3)SO_3Na\\(4)SO_3Na\\(5)NH_2\end{cases}$ (P = primuline base.)	From diazotised primuline.
Diamond Yellow G.	$C_6H_4\begin{cases}(4)CO_2H\\(2)N=N(2)C_6H_3\begin{cases}(4)CO_2H\\(5)OH\end{cases}\end{cases}$	From salicylic acid.
Chicago Orange.	$CH.C_6H_3\begin{cases}(1)NO\\(3)SO_3Na\end{cases}$ ‖ $CH.C_6H_3\begin{cases}(3)SO_3Na\\(1)N=N-C_6H_4.C_6H_4.NH_2\end{cases}$	From benzidine.
Arnica Yellow.	$CH.C_6H_3\begin{cases}(1)NO\\(3)SO_3Na\end{cases}$ ‖ $CH.C_6H_3\begin{cases}(3)SO_3Na\\(1)N=N-C_6H_4OH\end{cases}$	From *p*-aminophenol.

The dyes of the class of which xylidine scarlet is the type are very numerous, and are being continually added to. The characters of the dyes are materially dependent on their derivation from α or β-naphthol, and the exact nature of the isomeric naphthol-sulphonic acids employed also notably affects the colour and other properties of the dye. The letters R and G appended to the commercial names of the scarlets and other azo-dyes have reference to the sodium salts of the respective isomeric β-naphtholdisulphonic acids used for their production. "Salt G" yields the yellow shades, and "salt R" the red shades of the azo-dyes they are employed to produce. Similarly, where β-naphtholmonosulphonic acid is used, the characters of the resultant dyes depend to some extent on the isomer employed, whether "Schäffer's acid," "Bayer's acid," or other modifications.[1]

[1] Ref. Täuber and Norman. "Die Naphthalin-derivate".

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Yellow powder; orange solution.	Orange pp.	Grey pp.	Orange.	Grey pp.	Chrome dye for wool.
Yellow powder; yellow solution.	Green pp.	Orange pp.	Orange.	Orange.	Soluble in alcohol Chrome dye for wool.
Brown powder; orange solution.	No change.	Red pp.	Orange.	Red pp.	Direct dye for cotton.
Yellow paste; yellow solution.	....	....	Orange.	Yellow pp.	Soluble in alcohol. Chrome dye for wool.
Brown powder; orange solution.	Orange pp.	Brown pp.	Violet.	Brown pp.	Soluble in alcohol. Direct dye for cotton.
Brown powder; brown solution.	Red.	Brown pp.	Violet.	....	Direct dye for cotton.

Xylidine Red, Poncean R, Xylidine Scarlet, forms a scarlet-red powder, readily soluble in water or acetic acid, but less so in glycerine or alcohol. Its aqueous solution is unchanged by alkalies or dilute acids, and gives scarlet lakes with the acetates of lead and aluminum. Barium chloride precipitates it more perfectly, even in the presence of acetic acid. Xylidine Scarlet dyes animal fibres without a mordant in a slightly acid bath. The colour does not stand soaping, but is fast in the air, and resists the action of light fairly well.

Xylidine Red and allied colours are frequently adulterated with *dextrin*, which may be separated by treating the sample with sufficient alcohol. Tarry matters are sometimes precipitated on acidifying the solution of the dye with acetic acid.

Fast-Brown N.—This colouring matter, like others of similar constitution, dyes wool brown in an acid bath. It forms a dark brown

powder soluble in water to a yellowish-brown solution changed to brownish-red by sodium carbonate and giving a brown precipitate with hydrochloric acid. In strong sulphuric acid the dye dissolves with blue colour, a brown precipitate being formed on dilution.

Secondary Azo-Compounds. Tetrazo-dyes.

Amino-azobenzene may be regarded as a primary amine, since it contains the group NH_2. When this is acted on by nitrous acid a diazo-azobenzene compound is formed: $C_6H_5.N_2.C_6H_4NH_2HCl + NaNO_2 + HCl = C_6H_5.N_2.C_6H_4.N_2.Cl + NaCl + 2H_2O$. The product contains two $-N{:}N-$ groups and is called a secondary azo- or tetrazo-compound. By reaction with phenols in presence of alkalies, these tetrazo-compounds yield products of which several have received practical application, as they usually possess a colouring power superior to that of the azo-dyes of similar colour but simpler constitution. They are rendered soluble by sulphonation, the SO_3H group being often introduced into both chains. Thus by diazotising Acid Yellow, and acting with the product on sodium β-naphthol-α-sulphonate (Bayer's salt), *Croceïn Scarlet*, is obtained.

Crocein Scarlet, 3 B, or *Ponceau* 4 *RB*, is a dye of considerable practical importance. It forms a red-brown powder, soluble in water with a scarlet-red colour. The solution is turned violet-red by alkalies, but not precipitated except in very concentrated solutions. With hydrochloric acid it yields a yellowish-brown precipitate. With barium chloride it gives a red precipitate, becoming dark violet and crystalline on boiling. With calcium chloride the dye gives a flocculent red precipitate, which on boiling the liquid suddenly becomes brown and crystalline. When reduced with zinc in ammoniacal solution croceïn scarlet is decolourised, but the liquid acquires a yellow colour on exposure to air. The solid dye dissolves in strong sulphuric acid with indigo-blue colour, and on dilution a yellow-brown precipitate is formed, soluble in more water to a red solution.

Crocein Scarlet, 7 B, or *Ponceau* 6 *RB*, is homologous with the last and resembles it generally, but after reduction with zinc and ammonia the colourless liquid does not again become yellow on exposure to air. The hot concentrated aqueous solution, when treated with magnesium sulphate and allowed to stand, deposits on cooling long silky needles of the magnesium salt.

Ponceau S. extra is a disulphonated croceïn scarlet:

Orseillin 2 B is the isomeric compound from α-naphthol sulphonic acid.

Biebrich Scarlet, *Ponceau 3 R*, or *Azobenzene Red*, is a mixture *of Fast Scarlet or Double Scarlet*, with the corresponding disulphonate. It is a reddish-brown crystalline powder, forming a yellowish-red solution. The hot aqueous solution of Biebrich Scarlet becomes gelatinous on cooling. Dilute acids give a flocculent brownish-red precipitate in strong solutions. With zinc and ammonia the solution of Biebrich Scarlet is decolourised, but on exposure to air the liquid becomes yellow. The solid dye gives a green solution in strong sulphuric acid, and on adding water, the colour changes to blue, then to violet, and lastly, a dirty-brown precipitate is formed.

Scarlets 3 B, 3 R, and 4 R are varieties of Biebrich Scarlet.

Scarlet S, or *Ponceau SS extra*, is isomeric with Biebrich Scarlet, the β-naphthol being sulphonated instead of the amine. It is a brown powder, soluble in water with magenta-red colour. The solution yields a violet precipitate with hydrochloric acid, and is turned reddish-violet by sodium hydroxide.

Brilliant Croceïn M is a dye of the same composition prepared with sodium β-naphthol-γ-sulphonic acid instead of R. salt It is a light-brown powder, forming a cherry-red solution, which is turned brown by sodium hydroxide, and gives a brown precipitate with hydrochloric acid.

Azococcin 7 B and Croceïn B are colouring matters from naphthol analogous to Scarlet S. Azococcin 7 B is a difficultly soluble brown powder. The magenta coloured solution gives a brownish-red precipitate with hydrochloric acid, and with sodium hydroxide a violet-red precipitate soluble in water. Croceïn B is brown-red, difficultly soluble to a magenta-coloured solution which is precipitated violet by hydrochloric acid, and gives a violet colouration with sodium hydroxide. *Archil Red* is homologous with Scarlet S, containing two xylene-instead of two benzene-residues.

The tetrazo-dyes are characterised by their behaviour on reduction. With tin and hydrochloric acid, or other acid reducing agent, the decomposition is complete; but when treated with zinc and ammonia only partial decomposition ensues and the decolourised and filtered solution usually acquires a yellow colour on exposure to air, the colour-

less hydrazo-compound formed being oxidised to Acid Yellow and amino-azobenzene or some allied substance. (See below.)

A further distinction between the various red tetrazo-dyes containing a naphthol nucleus is to be found in their behaviour when treated in the solid state with strong sulphuric acid, as is shown in the following table:

Dye	Colour with sulphuric acid		Products of reduction	
	With conc. acid	On dilution with water	In alkaline solution	In acid solution
A — Biebrich Scarlet.	Green.	Blue, brown, and brown precipitate.	Amino-β-naphthol and amino-hydrazobenzene-disulphonic acid (oxidising with yellow colour).	Amino-β-naphthol, sulphanilic acid, and diamino-benzene-sulphonic acid.
Fast Scarlet.	Green.	Blue; then blue-red changing to scarlet.	Amino-β-naphthol para-diamino-benzene and amino-hydrazo-benzene sulphonic acid (oxidising with yellow colour).	
B — Scarlet S. Ponceau SS extra.	Violet.	Violet ppt.	Amino-β-naphthol-disulphonic acid and amino-azobenzene.	Sulphuric acid, amino-β-naphthol, aniline, and p:diamino-benzene.
Brilliant Croceïn M.	Reddish-violet.	Blue-violet; and red or brown ppt. on further dilution.		
Azococcin 7 B.	Bluish-violet.	Brownish-red ppt.		
Croceïn B.	Violet.	Violet ppt.		
C — Croceïn Scarlet 3 B.	Indigo-blue.	Yellow-brown ppt., and then red solution.	Amino-β-naphthol-α-sulphonic acid and amino-hydrazo-benzene-sulphonic acid (oxidising to Acid Yellow).	Sulphuric acid, amino-β-naphthol, sulphanilic acid, and p-diamino-benzene.
Croceïn Scarlet 7 B.	Blue.	Violet-red.		
Orseillin 2 B.	Blue.	Red.		
Ponceau S extra.	Blue.	Yellowish-red.		

Soudan III, or Amino-azobenzene-azo-β-naphthol. This is an unsulphonated tetrazo-dye of commercial interest. It forms a brown

powder insoluble in water, but soluble in alcohol. It dissolves in concentrated sulphuric acid with bluish-green colour, becoming blue on addition of water, and giving a red precipitate on further dilution.

Tetrazo-browns.—The following are among the colouring matters of this class which occur in commerce: Resorcin Brown, Fast Brown (Bayer), Acid Brown G, Acid Brown R, Fast Brown G (Tillman's), Fast Brown (Meister).

Resorcin Brown is a brown powder, soluble in water to a brown solution which is but slightly changed by sodium hydroxide, but yields a brown precipitate with hydrochloric acid. The solid dye dissolves in strong sulphuric acid with brown colour, and on dilution with water a brown precipitate is formed.

Acid Brown G is the type of several similar compounds obtained by introducing an amine residue instead of a phenol residue. It is prepared by the action of diazobenzene chloride on chrysoïdine-sulphonic acid. It dissolves in strong sulphuric acid with reddish-brown colour, becoming yellowish on dilution with water.

Acid Brown R is a similar dye prepared by the action of diazotised naphthionic acid on chrysoïdine. It is a brown powder, forming a brown aqueous solution which is unchanged by alkalies, but precipitated brown by acids. In strong sulphuric acid the dye dissolves with a dirty olive colour, and on dilution gives first a reddish and then a brown precipitate.

Fast Brown G is a brown powder, forming a reddish-brown solution. Dilute hydrochloric acid gives a violet precipitate, soluble in excess with a violet colour, or in water with a brown colour. Alkalies turn the aqueous solution cherry-red. Strong sulphuric acid dissolves the solid dye with a violet colour, becoming yellowish-brown on dilution.

Fast Brown of Meister, Lucius, and Brüning is homologous with the last dye, and forms a dark brown powder soluble in water with a brown colour. Alkalies turn the solution reddish-yellow, and dilute acids give a violet precipitate. Strong sulphuric acid dissolves the dye with a violet colour, becoming red on dilution. The colour produced on wool is a brownish-red.

Phenylene Brown. $C_6H_4\left<\begin{matrix} N_2—C_6H_3(NH_2)_2 \\ N_2—C_6H_3(NH_2)_2 \end{matrix}\right.$ .2HCl. This colouring matter, which is also known by the name of *Bismarck Brown*, *Vesuvine*, *Manchester Brown*, *Cinnamon Brown*, *Leather Brown*, etc., is the hydrochloride of benzene-diazophenylene-diamine. The com-

mercial product forms a dark brown powder always containing more or less common salt, and on solution in water often leaves a residue of insoluble impurities. The aqueous and alcoholic solutions are brown, but the liquid is turned red by a large excess of hydrochloric acid, though unchanged by slight excess. This reaction is characteristic. Ammonia and the fixed alkalies give a voluminous brown precipitate of the free base, which is somewhat soluble in boiling water, and more readily in alcohol, and when purified by recrystallisation forms small yellowish-red crystals which melt at 137°. Phenylene-Brown dissolves in strong sulphuric acid with reddish-brown colouration, becoming orange-red on dilution. The aqueous solution gives a brown precipitate with basic lead acetate (distinction from Chrysoïdine Orange), and is decolourised by treatment with a hydrochloric acid solution of stannous chloride.

Phenylene-Brown dyes wool a brownish-orange. It has been much used for dyeing leather.

Naphthol Black or **Azo-Black** contains $C_{10}H_5(SO_3Na)_2.N_2.$-$C_{10}H_6.N_2.C_{10}H_4(OH)\beta(SO_3Na)_2$, and results from the action of salt R on diazotised amino-azonaphthalene-disulphonic acid. It forms a readily soluble black powder, yielding a dark blue-violet aqueous solution; this forms a red-violet precipitate with hydrochloric acid, and with alkalies a blue precipitate soluble in much water. Precipitates are yielded with barium and calcium chlorides, as also by solutions of iron salts and some other metals. The dye dissolves in strong sulphuric acid with a dark green colour becoming blue on dilution. Naphthol Black dyes silk and wool a blue-black in a slightly acid bath.[1]

Wool Black is a similar dye produced by the action of diazotised amino-azobenzene-disulphonic acid on *p*-tolyl-β-naphthylamine, and has the formula, $C_6H_4(SO_3Na).N_2.C_6H_3(SO_3Na).N_2.C_{10}H_6.NH$-$(C_7H_7)$. It gives a violet precipitate with sodium carbonate and a red violet precipitate with hydrochloric acid, and dissolves in strong sulphuric acid with a blue colour, yielding a brown precipitate on dilution. Both Wool Black and Azo Black are employed as indigo-substitutes in wool-dyeing. They are fairly fast, and can be applied in a simple manner, by simply dyeing the wool in an acid bath, but the colour is apt to bleed in the milling process.

[1] Naphthol Black may be dyed on wool by first boiling the material in an acidified bath, then adding the dyestuff. It is very fast against the action of light, acids, and stoving, but only moderately fast to washing.

Naphthol Black 3 B has the formula $C_{10}H_5(NaSO_3)_2.N:N.C_{10}H_5\text{-}(SO_3Na)_2$. It occurs in the form of a crystalline powder, giving a dark blue solution in water. In strong sulphuric acid it dissolves with a black colour, changing to purple on dilution. The aqueous solution with hydrochloric acid shows no change, but sodium hydroxide turns it to a bluer colour. It is an acid dye for wool, giving deep navy blue shades which are quite fast to acids, alkalies, and light. There are several other naphthol blacks with similar characteristics to the above.

Naphthol Black 6 B has the formula $C_{10}H_5(SO_3Na)_2.N:N.C_{10}H_6\text{-}N:N.C_{10}H_4\begin{cases}(SO_3Na)_2\\OH.\end{cases}$ It differs from the 3 B brand in being soluble in alcohol, and dyeing a redder shade.

Naphthol Black 4 R has the same formula as the above, but is made from β-naphthol-γ-disulphonic acid whereas the former is prepared from β-naphthol-disulphonic acid R.

Naphthylamine Blacks are somewhat similar to the naphthol blacks just described. **Naphthylamine Black D** is a combination of amino-azo-naphthalene-disulphonic acid with a-naphthylamine. It dyes the animal fibres from a neutral bath giving black shades with a red tone, which are fairly fast to light and fulling.

Jet Black R is obtained by combining a-naphthylamine with diazotised benzene sodium disulphonate-azo-naphthylamine. Animal fibres are dyed from a neutral bath, giving black shades fairly fast to light and milling. **Jet Black G** is a very similar dyestuff prepared from the corresponding toluene derivative; it is dyed in the same manner as the former, but gives greener shades of black as fast as those of the R brand.

The tables on the following pages show the composition and properties of various tetrazo-dyes:

Commercial name	Formula	Remarks
Fast Brown.	$\begin{array}{l} C_6H_2(CH_3)_2.SO_3Na-N=N \\ C_6H_2(CH_3)_2.SO_3Na-N=N \end{array}>C_{10}H_5OH(\alpha)$	From 2 mols. xylidinesulphonic acid and α-naphthol.
Acid Brown R.	$\left.\begin{array}{l}NH_2(1)\\ NH_2(3)\end{array}\right\} C_6H_2 < \begin{array}{l} N=N-C_6H_5 \\ \left.\begin{array}{l}N=N(1)\\ SO_3Na(4)\end{array}\right\} C_{10}H_6\end{array}$	From naphthionic acid + Chrysoidine.
Soudan III.	$C_6H_4\left\{\begin{array}{l} N=N-C_6H_5 \\ N=N-C_{10}H_6OH(\beta)\end{array}\right.$	....
Acid Brown G.	$\left.\begin{array}{l}NH_2(1)\\ NH_2(3)\end{array}\right\} C_6H_2 < \begin{array}{l} N=N-C_6H_5 \\ (4)N=N-(1)C_6H_4(4)SO_3Na\end{array}$	From aniline + Chrysoidine.
Resorcin Brown.	$\left.\begin{array}{l}HO(1)\\ HO(3)\end{array}\right\} C_6H_2 < \begin{array}{l} (2)N=N-C_6H_3(CH_3)_2 \\ (4)N=N-(1)C_6H_4(4)SO_3Na\end{array}$	From xylidine + Tropæolin O.
Fast Brown G.	$HO(1)C_{10}H_5\left\{\begin{array}{l} (2)N=N(1)C_6H_4(4)SO_3Na \\ (4)N=N(1)C_6H_4(4)SO_3Na\end{array}\right.$	From sulphanilic acid + α-naphthol.
Fast Brown (Bayer).	$\left.\begin{array}{l}HO(1)\\ HO(3)\end{array}\right\} C_6H_2\left\{\begin{array}{l} (2)N=N(1)C_{10}H_6(4)SO_3Na \\ (4)N=N(1)C_{10}H_6(4)SO_3Na\end{array}\right.$	....
Phenylene Brown. Bismarck Brown. Manchester Brown.	$C_6H_4\left\{\begin{array}{l} (1)N=N-(1)C_6H_3\left\{\begin{array}{l}(2)NH_2HCl\\ (4)NH_2\end{array}\right. \\ (3)N=N-(1)C_6H_3\left\{\begin{array}{l}(2)NH_2HCl\\ (4)NH_2\end{array}\right.\end{array}\right.$	From diazotised *m*-phenylenediamine.
Tolylene Brown.	$C_6H_2\left\{\begin{array}{l} N=N-C_6H_2(NH_2)_2-N=N-C_{10}H_6.SO_3Na \\ CH_3 \\ SO_3Na \\ N=N-C_6H_2(NH_2)_2-N=N-C_{10}H_6.SO_3Na\end{array}\right.$	....
Benzo-Brown G.	$C_6H_4\left\{\begin{array}{l} (1)N=N-(4)C_6H_2\left\{\begin{array}{l}(1)NH_2\\ (2)N=N-(1)C_6H_4(4)SO_3Na\\ (3)NH_2\end{array}\right. \\ (3)N=N-(4)C_6H_2\left\{\begin{array}{l}(1)NH_2\\ (2)N=N-(1)C_6H_4(4)SO_3Na\\ (3)NH_2\end{array}\right.\end{array}\right.$	From Bismarck Brown.
Benzo-Brown B.	$C_6H_4\left\{\begin{array}{l} (1)N=N-(4)C_6H_2\left\{\begin{array}{l}(1)NH_2\\ (2)N=N-(1)C_{10}H_6(4)SO_3Na\\ (3)NH_2\end{array}\right. \\ (3)N=N-(4)C_6H_2\left\{\begin{array}{l}(1)NH_2\\ (2)N=N-(1)C_{10}H_6(4)SO_3Na\\ (3)NH_2\end{array}\right.\end{array}\right.$	From Bismarck Brown.
Catechu Brown.	$C_6H_4\left\{\begin{array}{l} (1)N=N-(4)C_6H_3\left\{\begin{array}{l}(3)NH_2\\ (1)N=N-(4)C_6H_3\left\{\begin{array}{l}(1)NH_2\\ (3)NH_2\end{array}\right.\end{array}\right. \\ (3)N=N-(4)C_6H_3\left\{\begin{array}{l}(3)NH_2\\ (1)N=N-(4)C_6H_3\left\{\begin{array}{l}(1)NH_2\\ (3)NH_2\end{array}\right.\end{array}\right.\end{array}\right.$	From Bismarck Brown.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; brown solution.	Orange.	Violet ppt.	Violet.	Red.	Liable to dye unevenly.
Brown powder; brown solution.	No change.	Brown ppt.	Green.	Brown ppt.	....
Brown powder; insoluble in water, soluble in alcohol.	....	....	Green.	Red ppt.	Used for colouring oils and varnishes.
Brown powder; brown solution.	No change.	No change.	Reddish-brown.	Yellowish-brown.	....
Brown powder; brown solution.	No change.	Brown ppt.	Brown.	Brown ppt.	Fast to light and milling on wool.
Brown powder; brown solution.	Red.	Violet ppt.	Violet.	Yellow.	....
Brown powder; brown solution.	Red.	Brown ppt.	Violet.	Red.	....
Brown powder; brown solution.	Brown ppt.	No change.	Brown.	Red.	Converted by reducing agents into phenylenediamine and triamino-benzene.
Dark brown powder; brown solution.	Orange ppt.	Brown ppt.	Violet.	Brown.	Direct cotton dye.
Dark brown powder; brown solution.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Direct cotton dye.
Dark brown powder; brown solution.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Direct cotton dye.
Brown powder; brown solution.	Brown ppt.	Brown ppt.	Brown.	Brown ppt.	Direct cotton dye.

Commercial name	Formula	Remarks
Direct Brown J.	$C_6H_4\begin{cases}(1)N=N-C_6H_3\begin{cases}(NH_2)_2\\N=N-C_6H_4.CO_2Na\end{cases}\\(3)N=N-C_6H_3\begin{cases}(NH_2)_2\\N=N-C_6H_4.CO_2Na\end{cases}\end{cases}$	From Bismarck Brown.
Cloth Red G. Azococcine 7B.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From N W acid.
Crocein B.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(2)C_{10}H_4\begin{cases}(1)OH\\(4)SO_3Na\\(8)SO_3Na\end{cases}\end{cases}$	From Sch. acid.
Brilliant Crocein. Cotton Scarlet.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{cases}\end{cases}$	From γ acid.
Ponceau SS extra.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-(1)C_{10}H_4\begin{cases}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}\end{cases}$	From R acid.
Ponceau 5 R. Erythrin X.	$C_6H_4\begin{cases}N=N-C_6H_5\\N=N-C_{10}H_3\begin{cases}OH\,\beta\\(SO_3Na)_3\end{cases}\end{cases}$	....
Crocein 3B.	$C_6H_3\begin{cases}N=N-C_6N_4.CH_3\\CH_3\\N=N-C_{10}H_4\begin{cases}OH(\alpha)\\(SO_3Na)_2\end{cases}\end{cases}$	From Sch. acid.
Cloth Red G. (Oehler).	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}\end{cases}$	From S acid.
ClothRed B (Oehler).	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(1)C_{10}H_4\begin{cases}(2(OH\\(3)SO_3Na\\(6)SO_3Na\end{cases}\end{cases}$	From R acid.
ClothRed B (Bayer).	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(2)C_{10}H_5\begin{cases}(1)OH\\(4)SO_3Na\end{cases}\end{cases}$	From N W acid.
Cloth Red 3 G.	$C_6H_3\begin{cases}N=N-C_6H_4.CH_3\\CH_3\\N=N-(1)C_{10}H_5\begin{cases}(2)NH_2\\(6)SO_3Na\end{cases}\end{cases}$	From Br. acid.
Bordeaux B X.	$C_6H_2\begin{cases}N=N-C_6H_3(CH_3)_2\\(CH_3)_2\\N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(6)SO_3Na\end{cases}\end{cases}$	From S acid.
Ponceau 4 R B. Crocein Scarlet 3 B.	$C_6H_4\begin{cases}N=N-(1)C_6H_4(4)SO_3Na\\N=N-(1)C_{10}H_5\begin{cases}(2)OH\\(8)SO_3Na\end{cases}\end{cases}$	From B acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Dark brown powder; brown solution.	No change.	Brown ppt.	Brown.	Brown ppt.	Direct cotton dye.
Brown powder; red solution.	Violet ppt.	Red ppt.	Violet.	Red ppt.	Precipitated from aqueous solution by Glauber's salt.
Red powder; red solution.	Violet.	Violet ppt.	Violet.	Violet ppt.	Acid dye for wool.
Brown powder; red solution.	Brown.	Brown ppt.	Violet.	Brown ppt.	Acid dye for wool.
Brown powder; red solution.	Violet.	Violet ppt.	Violet.	Violet ppt.	Acid dye for wool.
Brown powder; red solution.	Brown.	Brown ppt.	Violet.	Red.	Acid dye for wool.
Brown powder; red solution.	Violet.	Violet ppt.	Blue.	Red.	Acid dye for wool.
Brown powder; red solution.	Brown ppt.	Red ppt.	Blue.	Brown ppt.	But sparingly soluble in water. Dyes chromed wool.
Brown powder; red solution.	Red ppt.	Brown.	Blue.	Brown ppt.	Dyes chromed wool.
Red powder; red solution.	Violet.	Red ppt.	Blue.	Red ppt.	Dyes chromed wool.
Red powder; red solution.	No change.	Brown ppt.	Blue.	Red ppt.	Dyes chromed wool.
Brown powder; red solution.	Red ppt.	Red ppt.	Brown.	Brown ppt.	Acid dye for wool. Soluble in alcohol.
Brown powder; red solution.	Violet.	Brown ppt.	Blue.	Red.	Acid dye for wool.

Commercial name	Formula	Remarks
FastScarlet. Double Scarlet.	$C_6H_4\left\{\begin{array}{l} N=N-(1)C_6H_4(4)SO_3Na \\ N=N-(1)C_{10}H_6(2)OH \end{array}\right.$	....
Orchil Red A.	$C_6H_2\left\{\begin{array}{l} N=N-C_6H_3(CH_3)_2 \\ (CH_3)_2 \\ N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From R acid.
Bordeaux B X.	$C_6H_2\left\{\begin{array}{l} N=N-C_6H_2\left\{\begin{array}{l}(CH_3)_2\\SO_3Na\end{array}\right. \\ (CH_3)_2 \\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From S acid.
Bordeaux G.	$C_6H_3\left\{\begin{array}{l} N=N-C_6H_3\left\{\begin{array}{l}CH_3\\SO_3Na\end{array}\right. \\ CH_3 \\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From S acid.
Ponceau 6 R B. Crocein Scarlet 7 B.	$C_6H_3\left\{\begin{array}{l} N=N-C_6H_3\left\{\begin{array}{l}CH_3\\SO_3Na\end{array}\right. \\ CH_3 \\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(8)SO_3Na\end{array}\right.\end{array}\right.$	From B acid.
Biebrich Scarlet. Ponceau B. Ponceau 3 R B. Fast Ponceau B. New Red L. Imperial Scarlet.	$C_6H_3\left\{\begin{array}{l} N=N-(1)C_6H_4(4)SO_3Na \\ SO_3Na \\ N=N-(1)C_{10}H_6(2)OH \end{array}\right.$	....
Ponceau S extra. Fast Ponceau 2 B.	$C_6H_3\left\{\begin{array}{l} N=N-(1)C_6H_4(4)SO_3Na \\ SO_3Na \\ N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From R acid.
Orseillin B B.	$C_6H_3\left\{\begin{array}{l} N=N-C_6H_3\left\{\begin{array}{l}CH_3\\SO_3Na\end{array}\right. \\ CH_3 \\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Manchester Brown E E.	$C_6H_3\left\{\begin{array}{l} (3)N=N-(1)C_6H_2\left\{\begin{array}{l}(2)NH_2.HCl\\(4)NH_2\\(5)CH_3\end{array}\right. \\ (4)CH_3 \\ (1)N=N-(1)C_6H_2\left\{\begin{array}{l}(2)NH_2.HCl\\(4)NH_2\\(5)CH_3\end{array}\right.\end{array}\right.$	....
Naphthylene Red.	$C_{10}H_6\left\{\begin{array}{l} (1)N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right. \\ (5)N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From naphthionic acid.
Diamine Gold.	$C_{10}H_4\left\{\begin{array}{l} (1)N=N-(1)C_6H_4(4)OC_2H_5 \\ (3)SO_3Na \\ (7)SO_3Na \\ (5)N=N-(1)C_6H_4(4)OH \end{array}\right.$	....
Wool Black.	$C_6H_3\left\{\begin{array}{l} N=N-(1)C_6H_4(4)SO_3Na \\ SO_3Na \\ N=N-(1)C_{10}H_6(2)C_7H_7NH \end{array}\right.$	....

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown crystals; red solution.	Brown ppt.	Yellow.	Green.	Red.	Acid dye for wool.
Brown powder; violet solution.	Brown ppt.	Red ppt.	Blue.	Brown ppt.	Acid dye for wool.
Brown powder; red solution.	Browner.	Brown ppt.	Green.	Red ppt.	Acid dye for wool. Soluble in alcohol.
Brown powder; red solution.	Violet.	Red ppt.	Blue.	Red ppt.	Acid dye for wool. Soluble in alcohol.
Brown powder; red solution.	Violet ppt.	Red ppt.	Blue.	Violet.	Acid dye for wool.
Brown powder; orange solution.	Red ppt.	Red ppt.	Green.	Red ppt.	Acid dye for wool.
Brown powder; red solution.	Violet ppt.	No change.	Blue.	Orange.	Acid dye for wool.
Brown powder; red solution.	Yellower.	Violet.	Blue.	Red.	Acid dye for wool.
Brown powder; brown solution.	Brown ppt.	Brown.	Brown.	Brown.	Soluble in alcohol.
Red powder; red solution.	No change.	Black ppt.	Blue.	Black ppt.	Direct dye for cotton.
Orange powder; yellow solution in hot water.	Yellow ppt.	Yellow ppt. Black with excess.	Violet.	Green.	Direct dye for cotton. Soluble in alcohol.
Black powder; violet solution.	Violet ppt.	Violet ppt.	Blue.	Brown ppt.	Acid dye for wool.

Commercial name	Formula	Remarks
Fast Violet R.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-(1)C_6H_4(4)SO_3Na\\(1)N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From S acid.
Jet Black R.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_6H_3(SO_3Na)_2\\(1)N=H-(1)C_{10}H_6(4)NHC_6H_5\end{array}\right.$	....
Diamond Black.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_6H_3\left\{\begin{array}{l}OH\\CO_2Na\end{array}\right.\\(1)\ N=N-(2)\ C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Azonigrin.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_6H_2\left\{\begin{array}{l}OH\\(SO_3Na)_2\end{array}\right.\\(1)N=N-(1)C_{10}H_6(2)OH\end{array}\right.$	....
Naphthylamine Black D.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_{10}H_5(SO_3Na)_2\\(1)N=N-(1)C_{10}H_6(4)NH_2\end{array}\right.$	....
Napthol Black6B. Brilliant Black B.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_{10}H_5(SO_3Na)_2\\(1)N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From R acid.
Anthracite Black B.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_{10}H_5(SO_3Na)_2\\(1)N=N-(1)C_6H_3\left\{\begin{array}{l}(2)NHC_6H_5\\(4)NHC_6H_5\end{array}\right.\end{array}\right.$	....
Azo-Black. Blue-Black B.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_{10}H_6.SO_3Na\\(1)N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.$	From R acid.
Violet-Black.	$C_6H_4\left\{\begin{array}{l}(1)N=N-(1)C_{10}H_6(4)NH_2\\(4)N=N-(2)\ C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Naphthol Blue-Black.	$C_{10}H_2\left\{\begin{array}{l}N=N-C_6H_5\\(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\\N=N-(1)C_6H_4(4)NO_2\end{array}\right.$	From H acid.
Victoria Black B.	$C_{10}H_6\left\{\begin{array}{l}(1)N=N-(1)C_6H_4(4)SO_3Na\\(4)\ N=N\ -\ (4)\ C_{10}H_4\left\{\begin{array}{l}(1)OH\\(8)OH\\SO_3Na\end{array}\right.\end{array}\right.$	....
Fast Violet B.	$C_{10}H_6\left\{\begin{array}{l}(4)N=N-C_6H_3\left\{\begin{array}{l}CH_3\\SO_3Na\end{array}\right.\\(1)N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(6)SO_3Na\end{array}\right.\end{array}\right.$	....
Clayton Wool Brown.	$C_6H\left\{\begin{array}{l}(1)NH_2\\(2)NH_2\\N=N-C_6H_5\\N=N-C_6H_4SO_3Na\\N=N-C_{10}H_6SO_3Na\end{array}\right.$	....
Cloth Red 3 B extra.	$C_6H_4\left\{\begin{array}{l}(2)CH_3\\(1)N=N(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH.C_2H_5\\(7)SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$	From delta-acid.

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Green powder; violet solution.	Brown ppt.	Violet ppt.	Blue.	Violet ppt.	Acid dye for wool. Soluble in alcohol.
Black powder; violet solution.	Violet ppt.	Black ppt.	Blue.	Blue ppt.	Acid dye for wool. Soluble in alcohol.
Black powder; violet solution.	Blue.	Violet ppt.	Green.	Violet ppt.	Soluble in alcohol. Dyes chromed wool.
Black powder; black solution.	No change.	Red.	Greenish.	Red ppt.	Acid dye for wool.
Black powder; black solution.	No change.	Black ppt.	Bluish.	Black ppt.	Acid dye for wool.
Black powder; violet solution.	Blue.	No change.	Greenish.	Violet ppt.	Acid dye for wool.
Black powder; violet solution.	No change.	Violet ppt.	Black.	Greenish.	Acid dye for wool.
Black powder; violet solution.	Blue ppt.	Blue ppt.	Green.	Blue ppt.	Acid dye for wool.
Bronze powder; red solution.	Violet.	Violet ppt.	Blue.	Violet ppt.	Direct dye for cotton. Precipitated by magenta.
Black powder; blue solution.	No change.	Blue ppt.	Green.	Blue ppt.	Soluble in alcohol.
Black powder; violet solusolution.	Bluer.	Redder.	Blue.	Reddish.	Acid dye for wool.
Brown powder; violet tion.	Violet ppt.	Violet ppt.	Green.	Violet ppt.	Soluble in alcohol. Acid dye for wool.
Brown powder; brown solution.	No change.	No change.	....	....	....
Brown powder; red solution.	Brown ppt.	Brown ppt.	Green.	Red.	Soluble in alcohol. Acid dye for wool.

Commercial name	Formula	Remarks
Fast Azo-Granat. Fast Ponceau.	$C_6H_4\left\{\begin{array}{l}(2)CH_3\\(1)N=N(1)C_6H_3\left\{\begin{array}{l}(3)CH_3\\(4)N=N-(1)C_{10}H_6(2)OH\end{array}\right.\end{array}\right.$	Developed on fibre.
Milling Orange.	$C_6H_4\left\{\begin{array}{l}(2)SO_3Na\\(5)N=N-(3)C_6H_4(6)N=N-(2)C_6H_3\left\{\begin{array}{l}(4)CO_2H\\(5)OH\end{array}\right.\end{array}\right.$	From salicylic acid.
Leather Brown.	$C_6H_4\left\{\begin{array}{l}(1)NHC_2H_3O\\(4)N=N(1)C_6H_2\left\{\begin{array}{l}(2)NH_2\\(4)NH_2\\(5)N=N-(1)C_6H_4(4)NHC_2H_3O\end{array}\right.\end{array}\right.$	....
Heligoland Yellow.	$C_6H_4\left\{\begin{array}{l}(1)OH\\(4)N=N(1)C_6H_4(4)NH.CS.NH.C_6H_4.N=N.C_6H_4OH\end{array}\right.$	....
Tolylene Yellow.	$C_6H_2\left\{\begin{array}{l}(1)NH_2\\(3)NH_2\\(6)NO_2\\(4)N=N(1)-C_6H_2\left\{\begin{array}{l}(2)CH_3\\(5)SO_3H\\(3)N=N(1)-C_6H_2\left\{\begin{array}{l}(2)NH_2\\(4)NH_2\\(5)NO_2\end{array}\right.\end{array}\right.\end{array}\right.$	Tolylene diamine sulphonic acid and *m*-nitrophenylene diamine.
Janus Red.	$C_6H_4\left\{\begin{array}{l}(1)N(CH_3)_3Cl\\(3)N=N(1)C_6H_3\left\{\begin{array}{l}(2)CH_3\\(4)N=N(1)C_{10}H_6(2)OH\end{array}\right.\end{array}\right.$	From amino-phenyl-*m*-trimethyl ammonium chloride.
Diphenyl Chrysoin RR.	$C_6H_3\left\{\begin{array}{l}(1)NO\\(3)SO_3Na\\(4)CH=CH(1)C_6H_3\left\{\begin{array}{l}(2)SO_3Na\\(4)N=N(1)C_6H_4(4)N=N(1)C_6H_4(4)OC_2H_5\end{array}\right.\end{array}\right.$	From ethylation of tetrazo dye from nitroso-stilbene disulphonic acid.
Diphenyl Fast Brown G.	$C_6H_3\left\{\begin{array}{l}(1)NO\\(3)SO_3Na\\(4)CH=CH(1)C_6H_3\left\{\begin{array}{l}(2)SO_3Na\\(4)N=N(1)C_6H_4(4)N=N(2)C_{10}H_4\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(7)NH.C_6H_5\end{array}\right.\end{array}\right.\end{array}\right.$	From nitroso-stilbene disulphonic acid.
Diphenyl Catechin G.	$C_6H_3\left\{\begin{array}{l}(1)NO\\(3)SO_3Na\\(4)CH=CH(1)C_6H_3\left\{\begin{array}{l}(2)SO_3Na\\(4)N=N(1)C_6H_4(4)N=N(2)C_{10}H_4\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(7)N(CH_3)_2\end{array}\right.\end{array}\right.\end{array}\right.$	From nitroso-stilbene disulphonic acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; insoluble.	Violet with alcohol solution.	....	Green.	Red ppt.	Soluble in alcohol. Ingrain colour.
Brown powder; orange solution.	Red ppt.	Yellow ppt.	Violet.	Yellow ppt.	Chrome dye for wool.
Black powder; brown solution.	Brown ppt.	Darker.	Brown.	....	Dye for leather.
Brown powder; yellow solution.	Redder.	Brown ppt.	Orange.	Brown ppt.	Direct dye for cotton.
Yellow powder; yellowish-brown solution.	Brown ppt.	Brown ppt.	Brown.	Brown ppt.	Dyes cotton from neutral bath.
Red-brown powder; red solution.	Bluish-violet ppt.	Brownish-red ppt.	Green.	Red ppt.	Dyes cotton on tannin and antimony mordant.
Reddish-brown powder; reddish orange solution.	Reddish-brown ppt.	Brownish-black ppt.	Pure blue.	Brownish-black ppt.	Dyes unmordanted cotton.
Dark brown powder; yellowish brown solution.	Dark brown ppt.	Brownish black ppt.	Dark blue.	Brownish-black ppt.	Dyes unmordanted cotton.
Dark brown powder; yellowish-brown solution.	Dark brown ppt.	Dark brown ppt.	Blackish-violet blue.	Brownish-black ppt.	Dyes unmordanted cotton.

Polyazo-dyestuffs.—Many azo-dyestuffs containing 3, 4 and more azo-groups in the molecule are now manufactured and range in shade from violet to blue, green or black. As an example of these substances *Chrome Patent Green* may be cited, prepared by combining G acid, which is 1-amino-8 naphthol-4.6-disulphonic acid, successively with the diazotised dyestuff from diazotised amino-salicylic acid and α-naphthylamine, and with diazo-benzene. Thus it has the formula:

$$C_6H_3(COOH)(OH).N_2.C_{10}H_6.N_2.C_{10}H_2(NH_2)(OH)-(SO_3Na)_2.N_2.C_6H_5.$$

It is a chocolate-brown powder, soluble in water to a greenish blue solution, which gives a blue precipitate with hydrochloric acid and a bluish-violet precipitate with sodium hydroxide solution. In strong sulphuric acid it dissolves to a green solution which forms a black precipitate on dilution. It dyes wool to a dark bluish-green shade by the one bath method.

Direct Cotton (Benzidine) Dyestuffs.

These possess the characteristic property of dyeing cotton in a neutral or alkaline bath without a mordant. They all contain a sulpho- or carboxyl group, and occur in commerce as sodium salts.

As already stated, all the colouring matters of this class dye cotton in a neutral or slightly alkaline bath without the aid of a mordant. In practice, the cotton is boiled in a solution of dye rendered alkaline by soap and sodium phosphate and carbonate. Borate, silicate, and stannate of sodium are also used.

The benzidine dyes can also be used for wool, but an alkaline bath is an objection. With some of them a bath acidified with acetic acid can be employed. An after-treatment with copper sulphate solution also renders many of the benzidine colours faster to light on wool.

The fastness against light and fulling of a number of the benzidine colours may be materially increased when dyed on cotton by a subsequent treatment with such metallic salts as copper sulphate, chromium fluoride, and potassium dichromate. In some cases the shade is not much altered by this process, while in others it is changed considerably, generally being rendered duller.

The following tables show the constitution and reactions of important dyes obtained from benzidine and its analogues.

The direct cotton dyes can be fixed on silk from a bath containing soap and sodium chloride; and mixed silk and cotton goods can be dyed with these colours in one bath.

The benzidine dyes act as mordants to the basic aniline dyes.

The following is a detailed description of some of the more important dyes from benzidine and its analogues:

Chrysamin G, or **Flavophenin** is produced by the action of tetrazodiphenyl chloride on sodium salicylate. It is sparingly soluble in cold but readily in boiling water. The solution has an orange colour, changed by sodium hydroxide to an orange-red, from which acids precipitate tetrazodiphenyl-disalicylic acid in orange flakes soluble in ether.[1] Chrysamin is very sensitive to the action of copper compounds, its colour being darkened to a brown. Chrysamin differs from most of the other benzidine dyes in that its shades are very fast to light and soap.

Congo-red forms a brownish-red powder, readily soluble in water to produce a blood-red solution. Very small quantities of dilute acids turn the liquid blue. Alkalies restore the red colour, and salts of neutral constitution, such as alum, ferrous sulphate, cupric sulphate, etc., do not act as acids. Hence it has been proposed to employ Congo-red as an indicator, but it has been shown by R. T. Thompson (*J. Soc. Chem. Ind.*, 1887, **6**, 195) that its delicacy has been overrated. While not wholly unaffected by weak acids, such as carbonic and sulphydric, it fails to indicate the presence of acetic acid in presence of 12 times the quantity of sodium acetate. Congo-red dissolves in strong sulphuric acid with slate-blue colour, which is not changed by dilution. Congo-red dyes cotton a bright crimson-red, but the colour is far from permanent. On wool the colour is rather more scarlet, brighter, and more stable than on cotton.

Benzopurpurin 4 B is the next higher homologue of Congo-red. It forms a dark brownish-red powder, soluble in water with orange-red colour, which is unchanged by alkalies. From strong solutions, dilute acids throw down a reddish-brown precipitate resembling ferric hydroxide. In a hot bath containing soap or alkaline carbonate, benzopurpurin dyes cotton a fine scarlet. The colour is almost unaffected by dilute acids, and is much faster to light than Congo-red.

[1] The naphthol-azo colours have been employed in the colouration of sand for experimental purposes in hydraulic engineering, where it is desirable to use sand of different colours, which colours must resist the action of water and friction fairly well. The dyes are dissolved in sodium hydroxide, and the sand is treated with the diluted solution.

Commercial name	Formula	Remarks
From Benzidine. Chrysamin G. Flavophenin.	$C_6H_4-N=N-(4)C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2H\end{matrix}\right.$ $C_6H_4-N=N-(4)C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2H\end{matrix}\right.$	From salicylic acid.
Congo Yellow.	$C_6H_4-N=N-NH(4)C_6H_4(1)SO_3Na$ $C_6H_4-N=N-(4)C_6H_4(1)OH$	From sulphanilic acid and phenol.
Congo Red.	$C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$	From naphthionic acid.
Brilliant Congo G.	$C_6H_4-N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)NH_2\\(6)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(1)C_{10}H_4\left\{\begin{matrix}(6)SO_3Na\\(3)SO_3Na\\(2)NH_2\end{matrix}\right.$	From R acid.
Sulphanil Yellow. Parasulphurin S.	$C_6H_4-N=N-NH(4)C_6H_4(1)SO_3Na$ $C_6H_4-N=N-NH(4)C_6H_4(1)SO_3Na$	From sulphanilic acid.
Azo-orseillin.	$C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)OH\\(4)SO_3Na\end{matrix}\right.$	From N W acid.
Bordeaux Extra. Congo Violet. Bordeaux C O V.	$C_6H_4-N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)OH\\(6)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)OH\\(6)SO_3Na\end{matrix}\right.$	From β acid.
Congo Corinth G.	$C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$	From N W acid.
Congo G.	$C_6H_4-N=N-NH(1)C_6H_4(3)SO_3Na$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$	From sulphanilic and naphthionic acid.
Alkali Red.	$C_6H_4-N=N-C_{10}H_4\left\{\begin{matrix}NH_2(\alpha)\\(SO_3Na)_2\end{matrix}\right.$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$	From naphthylaminedisulphonic and naphthionic acids.
Congo P.	$C_6H_4-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(1)C_6H_4(4)OH$	From G acid.
Direct Red B. Diamine Scarlet B.	$C_6H_4-N=N-(1)C_6H_4(4)OC_2H_5$ $C_6H_4-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(6)SO_3Na\\(8)SO_3Na\end{matrix}\right.$	From G acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; yellow solution.	Brown.	Brown ppt.	Violet.	Brown ppt.	Brown ppt. with acetic acid.
Yellow paste; yellow solution.	Brown.	Brown ppt.	Red.	Brown ppt.	Brown ppt. with acetic acid.
Brown powder; brown solution.	Brown ppt.	Blue ppt.	Blue.	Blue ppt.	Violet ppt. with acetic acid.
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	Precipitated by magenta.
Yellow paste; yellow solution.	No change.	....	Decomposed, nitrogen evolved on heating.	....	....
Violet paste; violet solution.	Red.	Violet ppt.	Blue.	Violet ppt.	....
Brown powder; red solution.	Yellower.	Violet ppt.	Violet.	Violet ppt.	....
Black powder; red solution.	Redder.	Violet ppt.	Blue.	Violet ppt.	Violet solution with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Blue ppt.	Blue.	Blue ppt.	Violet ppt. with acetic acid.
Red powder; red solution.	No change.	Blue ppt.	Blue.	Violet ppt.	Slightly soluble in alcohol Obsolete.
Red powder; red solution.	Brown.	Brown ppt.	Violet.	Brown.	Soluble in alcohol.
Red crystals; red solution.	No change.	Brown.	Violet.	Brown.	Soluble in alcohol. Acid dye for wool.

Commercial name	Formula	Remarks
Cloth Orange.	$\begin{array}{l} C_6H_4-N=N-C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2H\end{array}\right.\\ C_6H_4-N=N-(4)C_6H_3\left\{\begin{array}{l}(1)OH\\(3)OH\end{array}\right.\end{array}$	From salicylic acid.
Benzo Orange R.	$\begin{array}{l} C_6H_4-N=N-C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\\ C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}$	From salicylic acid.
Cloth Brown G.	$\begin{array}{l} C_6H_4-N=N-C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2H\end{array}\right.\\ C_6H_4-N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(7)OH\end{array}\right.\end{array}$	From salicylic acid.
Cloth Brown R.	$\begin{array}{l} C_6H_4-N=N-C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\\ C_6H_4-N=N-C_{10}H_5\left\{\begin{array}{l}SO_3Na\\OH\end{array}\right.\end{array}$	From salicylic acid.
Carbazol Yellow.	$\begin{array}{l} C_6H_3-N=N-C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\\ \quad >NH\\ C_6H_3-N=N-C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\end{array}$	From salicylic acid.
Congo Brown R.	$\begin{array}{l} C_6H_4-N=N-(4)C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\\ C_6H_4-N=N-(4)C_6H_2\left\{\begin{array}{l}(1)OH\\(3)OH\\(2)N=N-(1)C_{10}H_6(4)SO_3Na\end{array}\right.\end{array}$	From Cloth Orange with naphthionic acid.
Congo Brown G.	$\begin{array}{l} C_6H_4-N=N-(4)C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\\ C_6H_4-N=N-(4)C_6H_2\left\{\begin{array}{l}(1)OH\\(3)OH\\(2)N=N-(1)C_6H_4(4)SO_3Na\end{array}\right.\end{array}$	From Cloth Orange with sulphanilic acid.
Hessian Brown B B.	$\begin{array}{l} C_6H_4-N=N-(2)C_6H_2\left\{\begin{array}{l}(1)OH\\(3)OH\\(4)N=N-(1)C_6H_4(4)SO_3Na\end{array}\right.\\ C_6H_4-N=N-(2)C_6H_2\left\{\begin{array}{l}(1)OH\\(3)OH\\(4)N=N-(1)C_6H_4(4)SO_3Na\end{array}\right.\end{array}$	From Resorcin Yellow.
Benzo Grey.	$\begin{array}{l} C_6H_4-N=N-(2)C_6H_3\left\{\begin{array}{l}(1)OH\\(4)CO_2Na\end{array}\right.\\ C_6H_4-N=N-(4)C_{10}H_6(1)-N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)CO_2Na\end{array}\right.\end{array}$	From N W acid.
Direct Grey R.	$\begin{array}{l} C_6H_4-N=N-C_{10}H_3\left\{\begin{array}{l}(OH)_2\\CO_2Na\\SO_3Na\end{array}\right.\\ C_6H_4-N=N-C_{10}H_3\left\{\begin{array}{l}(OH)_2\\CO_2Na\\SO_3Na\end{array}\right.\end{array}$	From β-hydroxy-naphthoic acid.
Diamine Black R.	$\begin{array}{l} C_6H_4-N=N-C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(8)OH\\(6)SO_3Na\end{array}\right.\\ C_6H_4-N=N-C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(8)OH\\(6)SO_3Na\end{array}\right.\end{array}$	From G acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; brown solution.	Red ppt.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol. Dyes chromed wool.
Red crystals; orange solution.	Orange ppt.	Violet.	Violet.	Violet ppt.	....
Brown powder; brown solution.	Brown-red.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol. Dyes chromed wool.
Red powder; brown solution.	Red ppt.	Brown ppt.	Violet.	Brown ppt.	Dyes chromed wool.
Yellow powder; yellow solution.	Orange.	Brown ppt.	Blue.	Brown ppt.	....
Red powder; red solution.	Red.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol.
Brown powder; brown solution.	Red.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol.
Brown powder; brown solution.	Red.	Brown ppt.	Black.	Brown ppt.	Soluble in alcohol.
Grey powder; brown solution.	No change.	Black ppt.	Blue.	Black ppt.	....
Grey powder; violet solution.	Violet red.	Grey ppt.	Blue.	Grey ppt.	....
Black powder; violet solution.	No change.	Blue ppt.	Blue.	Blue ppt.	Soluble in alcohol.

Commercial name	Formula	Remarks
Diamine Fast Red.	$\begin{array}{l} C_6H_4-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)NH_2\\(8)OH\\(6)SO_3Na\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right. \end{array}$	From G acid.
Diamine Brown V.	$\begin{array}{l} C_6H_4-N=N-C_{10}H_4\left\{\begin{matrix}(2)NH_2\\(8)OH\\(6)SO_3Na\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-(4)C_6H_3\left\{\begin{matrix}(1)NH_2\\(3)NH_2\end{matrix}\right. \end{array}$	From G acid.
Diamine Violet N.	$\begin{array}{l} C_6H_4-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)NH_2\\(8)OH\\(6)SO_3Na\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)NH_2\\(8)OH\\(6)SO_3Na\end{matrix}\right. \end{array}$	From G acid.
Diamine Blue B B.	$\begin{array}{l} C_6H_4-N=N-C_{10}H_3\left\{\begin{matrix}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-C_{10}H_3\left\{\begin{matrix}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{matrix}\right. \end{array}$	From H acid.
Diamine Bronze G.	$\begin{array}{l} C_6H_4-N=N-C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-C_{10}H_3\left\{\begin{matrix}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)N=N(4)C_6H_3\left\{\begin{matrix}(3)NH_2\\(1)NH_2\end{matrix}\right.\end{matrix}\right. \end{array}$	From H acid.
Diamine Green B.	$\begin{array}{l} C_6H_4-N=N-(4)C_6H_4(1)OH \\ \vert \\ C_6H_4-N=N-C_{10}H_2\left\{\begin{matrix}(1)OH\\(2)NH_2\\(3)SO_3Na\\(6)SO_3Na\\N=N-(1)C_6H_4(4)NO_2\end{matrix}\right. \end{array}$	....
Sulphone Azurin.	$SO_2\begin{array}{l} \diagup C_6H_3\left\{\begin{matrix}SO_3Na\\N=N-(1)C_{10}H_6(2)NHC_6H_5\end{matrix}\right. \\ \vert \\ \diagdown C_6H_3\left\{\begin{matrix}N=N-(1)C_{10}H_6(2)NHC_6H_5\\SO_3Na\end{matrix}\right. \end{array}$	From benzidine sulphone.
Cotton Bordeaux.	$\begin{array}{l} C_6H_3\left\{\begin{matrix}N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.\\(2)\end{matrix}\right. \\ \vert \qquad >C=N-OH \\ C_6H_3\left\{\begin{matrix}(2)\\N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.\end{matrix}\right. \end{array}$	From diamino-diphenylene-ketoxime with naphthionic acid.
Diamine Red N O.	$\begin{array}{l} C_6H_3\left\{\begin{matrix}(3)OC_2H_5\\N=N-(1)C_{10}H_5\left\{\begin{matrix}(2)NH_2\\(6)SO_3Na\end{matrix}\right.\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-(1)C_{10}H_5\left\{\begin{matrix}(7)SO_3Na\\(2)NH_2\end{matrix}\right. \end{array}$	From ethoxy-benzidine.
Diamine Blue B.	$\begin{array}{l} C_6H_3\left\{\begin{matrix}(3)OC_2H_5\\N=N-(1)C_{10}H_4\left\{\begin{matrix}(2)OH\\(3)SO_3Na\\(7)SO_3Na\end{matrix}\right.\end{matrix}\right. \\ \vert \\ C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(4)SO_3Na\\(1)OH\end{matrix}\right. \end{array}$	From ethoxy-benzidine.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On Dilution with water	
Red powder; red solution.	No change.	Brown ppt.	Blue.	Brown ppt.	Soluble in alcohol.
Black powder; red solution in hot water.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Soluble in alcohol.
Brown powder; violet solution.	No change.	Black ppt.	Blue.	Violet ppt.	....
Grey powder; violet solution.	No change.	No change.	Blue.	Violet.	....
Black powder; brown solution in hot water.	Yellower.	Purple ppt.	Violet.	Black ppt.	....
Black powder; green solution.	Yellower.	Black ppt.	Violet.	Black ppt.	Soluble in alcohol.
Dark blue powder; blue solution.	Blue ppt.	Blue ppt.	Violet.	Violet ppt.	Soluble in alcohol.
Brown powder; violet solution.	Violet ppt.	Blue ppt.	Blue.	Blue ppt.	....
Green crystals; red solution.	No change.	Violet ppt.	Blue.	Black ppt.	Soluble in alcohol.
Bronze powder; blue solution.	Violet.	Blue ppt.	Blue.	Blue ppt.	....

Commercial name	Formula	Remarks
Diamine Blue 3 R.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}$	From ethoxybenzidine and N W acid.
Diamine Black B.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N=N-(5)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(8)OH\\(6)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_4-N=N-(5)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(8)OH\\(6)SO_3Na\end{array}\right.\end{array}$	From ethoxybenzidine and G acid.
Diamine Blue-black E.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)OH\\(3)SO_3Na\\(7)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_4-N=N-(5)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(8)OH\\(6)SO_3Na\end{array}\right.\end{array}$	From ethoxybenzidine and G acid.
Benzo-azurin G.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3NA\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From dianisidine and N W acid.
Azo-violet.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From dianisidine and N W acid.
Heliotrope.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NHC_2H_5\\(7)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NHC_2H_5\\(7)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From dianisidine and δ acid.
Benzo-azurin 3 G.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(5)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(5)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From dianisidine and L acid.
Benzo-purpurin 10 B.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From dianisidine and naphthionic acid.
Brilliant Azurin 5 G.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-C_{10}H_4\left\{\begin{array}{l}(1)OH\\(8)OH\\(4)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N=N-C_{10}H_4\left\{\begin{array}{l}(1)OH\\(8)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From dianisidine.
Diamine Sky Blue.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N=N-C_{10}H_3\left\{\begin{array}{l}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N=N-C_{10}H_3\left\{\begin{array}{l}(1)NH_2\\(8)OH\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From diphenetidine and H acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Black powder; violet solution.	Redder.	No change.	Blue.	Violet ppt.	Soluble in alcohol.
Black powder; blue solution.	No change.	Blue ppt.	Blue.	Violet ppt.	Soluable in alcohol. Yields ingrain colours.
Black powder; blue solution.	No change.	Blue ppt.	Blue.	Blue ppt.	....
Black powder; violet solution.	Red.	Violet ppt.	Blue.	Violet ppt.	Dyed colour becomes red on heating and blue again on cooling. Precipitated by magenta.
Blue powder; violet solution.	Red.	Blue ppt.	Blue.	Blue ppt.	Violet colour with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	Violet colour with acetic acid.
Black powder; violet solution.	Violet red.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol.
Red powder; red solution.	Red ppt.	Blue ppt.	Blue.	Blue ppt.	Soluble in alcohol.
Black powder; violet solution.	Red.	Blue ppt.	Greenish-blue.	Violet ppt.	Soluble in alcohol.
Grey powder; blue solution.	Redder.	No change.	Green.	Blue.	....

Commercial name	Formula	Remarks
Benzo Black Blue G.	$C_6H_3\left\{\begin{array}{l}SO_3Na\\ N{=}N-(4)C_{10}H_6(1)N{=}N(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}SO_3Na\\ N{=}N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
New Red.	$C_6H_3\left\{\begin{array}{l}(2)NO_2\\ N{=}N-(4)C_6H_3\left\{\begin{array}{l}(1)OH\\(2)CO_2Na\end{array}\right.\end{array}\right.$ $C_6H_4-N{=}N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.$	From nitrobenzidine.
Direct Blue B.	$C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N{=}N-C_{10}H_3\left\{\begin{array}{l}(OH)_2\\SO_3Na\\CO_2Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OCH_3\\ N{=}N-C_{10}H_5\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right.\end{array}\right.$	From dianisidine.
Benzo Indigo blue.	$C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N{=}N-(4)C_{10}H_6(1)NH_2\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)OC_2H_5\\ N{=}N-(4)C_{10}H_4\left\{\begin{array}{l}SO_3Na\\(1)OH\\(8)OH\end{array}\right.\end{array}\right.$	From ethoxybenzidine.
Glycin Corinth.	$C_6H_4-N{=}N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$ $C_6H_4-N{=}N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$	....
Glycin Red.	$C_6H_4-N{=}N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$ $C_6H_4-N{=}N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.$	....
Glycin Blue.	$C_6H_3-N{=}N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$ $>SO_2$ $C_6H_3-N{=}N-(1)C_{10}H_6(4)NH.CH_2.CO_2Na$	....
Heliotrope 2 B.	$C_6H_4-N{=}N-(1)C_{10}H_5\left\{\begin{array}{l}(2)OH\\(8)SO_3Na\end{array}\right.$ $C_6H_4-N{=}N-(2)C_{10}H_4\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\\(8)SO_3Na\end{array}\right.$	From Sch. acid.
Rouge M.	$C_6H_4-N{=}N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\(4)OH\end{array}\right.$ $C_6H_4-N{=}N-(2)C_{10}H_4\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.$	....
Oxamine Violet.	$C_6H_4-N{=}N-(2)C_{10}H_4\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(6)NH_2\end{array}\right.$ $C_6H_4-N{=}N-(2)C_{10}H_4\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(6)NH_2\end{array}\right.$	....
Anthracene Red.	$C_6H_3\left\{\begin{array}{l}(3)NO_2\\ N{=}N-(1)C_6H_3\left\{\begin{array}{l}(3)CO_2Na\\(4)OH\end{array}\right.\end{array}\right.$ $C_6H_4-N{=}N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.$	From salicylic and N W acids.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Black powder; blue black solution.	Blue.	Blue ppt.	Green.	Blue ppt.	....
Red powder; red solution in hot water.	No change.	Red ppt.	Red.	Orange.	Acid or chrome dye for wool.
Black powder; blue solution.	Violet.	Black ppt.	Blue.	Violet ppt.	Soluble in alcohol.
Grey powder; blue solution.	Violet ppt.	Blue ppt.	Blue.	Blue ppt.	....
Brown powder; violet solution.	Red ppt.	Violet ppt.	Blue.	Violet ppt.	Soluable in alcohol. Direct dye for cotton.
Brown powder; orange solution.	Orange ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Dark powder; red solution.	Red ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Grey powder; violet solution.	Redder.	Violet ppt.	Blue.	Violet.	Soluble in alcohol. Direct dye for cotton.
Red powder; red solution.	Orange.	Brown ppt.	Blue.	Colourless.	Direct dye for cotton.
Green powder; violet solution.	Violet ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Brown powder; red solution.	No change.	Red ppt.	Red.	Brown ppt.	Soluble in alcohol. Acid and chrome dye for wool.

Commercial name	Formula	Remarks
Dianisidine Blue.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)O.CH_3\\ N=N-(1)C_{10}H_6(2)OH\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)O.CH_3\\ N=N-(1)C_{10}H_6(2)OH\end{array}\right.\end{array}$	Developed on the fibre.
Diamine Pure Blue. Benzo and Congo Pure Blues.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)O.CH_3\\ N=N-(2)C_{10}H_3\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)NH_2\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)O.CH_3\\ N=N-(2)C_{10}H_3\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)NH_2\end{array}\right.\end{array}\right.\end{array}$	From H acid.
Tolylene Brown G.	$\begin{array}{l} N-(2)C_6H_2\left\{\begin{array}{l}(1)CH_3\\(5)SO_3Na\\(4)N\end{array}\right. \\ \Vert \qquad\qquad\qquad\quad \Vert \\ N-(2)C_6H_2\left\{\begin{array}{l}(4)N\\(5)NH_2\\(1)NH_2\end{array}\right.\end{array}$	....
Tolylene Orange R. R.	$C_6H_2\left\{\begin{array}{l}(2)N=N-(1)C_{10}H_6(2)NH_2\\(3)SO_3Na\\(5)CH_3\\(6)N=N-(1)C_{10}H_6(2)NH_2\end{array}\right.$	....
Dianil Black.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}SO_3Na\\ N=N(1)-C_{10}H_4\left\{\begin{array}{l}(2)N=N-C_6H_3(NH_2)_2\\(6)SO_3Na\\(8)OH\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_4-N=N(1) \\ \qquad\quad \vert \\ \quad C_{10}H_4\left\{\begin{array}{l}(2)N=N-C_6H_3(NH_2)_2\\(6)SO_3Na\\(8)OH\end{array}\right.\end{array}$	From γ acid.
Pyramine Orange.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(2)SO_3Na\\ N=N-(1)C_6H_2\left\{\begin{array}{l}(2)NH_2\\(4)NH_2\\(5)NO_2\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(2)SO_3Na\\ N=N-(1)C_6H_2\left\{\begin{array}{l}(2)NH_2\\(4)NH_2\\(5)NO_2\end{array}\right.\end{array}\right.\end{array}$	....
Diamine Catechin.	$C_{10}H_4\left\{\begin{array}{l}(1)N=N-(1)C_{10}H_6(4)OH\\(3)SO_3H\\(7)SO_3H\\(5)N=N-(1)C_{10}H_6(4)OH\end{array}\right.$	From diazotised Naphthylene Violet; developed on the fibre.
Naphthyl Blue 2B.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)CO_2Na\\ N=N-C_{10}H_4\left\{\begin{array}{l}(1)NH.CO.C_6H_5\\(8)OH\\(5)SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)CO_2Na\\ N=N-C_{10}H_4\left\{\begin{array}{l}(1)NH.CO.C_6H_5\\(8)OH\\(5)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From ortho-diamino-diphenic acid.
Benzo Olive.	$\begin{array}{l} C_6H_4-N=N-(1)C_6H_3\left\{\begin{array}{l}(3)CO_2Na\\(4)OH\end{array}\right. \\ \vert \\ C_6H_4-N=N-(1)C_{10}H_6(4)N=N-C_{10}H_3\left\{\begin{array}{l}OH\\NH_2\\(SO_3Na)_2\end{array}\right.\end{array}$	From H acid.
Benzo black Blue 5 G.	$\begin{array}{l} C_6H_3\left\{\begin{array}{l}(3)SO_3Na\\ N=N-C_{10}H_4\left\{\begin{array}{l}(OH)_2\\SO_3Na\end{array}\right.\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}(3)SO_3Na\\ N=N-C_{10}H_6(4)N=N-C_{10}H_4\left\{\begin{array}{l}(OH)_2\\SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From S acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
....	....	....	....	....	Ingrain colour.
Black powder; blue solution.	Redder.	No change.	Green.	Blue.	Direct dye for cotton.
Brown powder; brown solution.	No change.	Brown ppt.	Red.	....	Direct dye for cotton.
Red powder; orange solution.	Orange ppt.	Brown ppt.	Blue.	....	Soluble in alcohol. Direct dye for cotton.
Black powder; soluble in water.	Precipitate.	Precipitate.	Dark blue.	Black ppt.	Direct cotton dye.
Red powder; orange solution.	Orange ppt.	Orange ppt.	Yellow.	Orange ppt.	Direct dye for cotton.
....	....	....	....	....	Ingrain colour.
Blue powder; blue solution.	Violet.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Black powder; green solution.	Brown.	Green ppt.	Violet.	Black ppt.	Direct dye for cotton.
Grey powder; blue solution.	No change.	Green ppt.	Green.	Green ppt.	Direct dye for cotton.

Commercial name	Formula	Remarks
Alizarin Yellow F S.	$M\left\{\begin{matrix} N=N-C_6H_3\left\{\begin{matrix}OH\\CO_2Na\end{matrix}\right. \\ N=N-C_6H_3\left\{\begin{matrix}OH\\CO_2Na\end{matrix}\right. \\ N=N-C_6H_3\left\{\begin{matrix}OH\\CO_2Na\end{matrix}\right. \end{matrix}\right.$ (M = magenta base.)	From Magenta and salicylic acid.
Mekong Yellow G.	$C_6H_4-N=N-C_6H_3\left\{\begin{matrix}OH\\CO_2Na\end{matrix}\right.$ $\begin{matrix}C_6H_4-N=N-C_6H_3OH\\C_6H_4-N=N-C_6H_3OH\end{matrix}\Big\}CH_2$ $C_6H_4-N=N-C_6H_3\left\{\begin{matrix}OH\\CO_2Na\end{matrix}\right.$	From salicylic acid.
From Diamino-phenyl-tolyl. Direct Yellow.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_6H_3\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right.$ $C_6H_4-N=N-C_6H_3\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right.$	From salicylic acid.
Direct Red.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(2)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$ $C_6H_4-N=N-(2)C_{10}H_5\left\{\begin{matrix}(1)NH_2\\(4)SO_3Na\end{matrix}\right.$	From naphthionic acid.
Diamine Yellow W.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_6H_3\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(4)CO_2H\end{matrix}\right.$ $C_6H_4-N=N-(4)C_6H_4(1)OC_2H_5$	From salicylic acid.
From Tolidine. Chrysamine R.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_6H_3\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right.$ $C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-C_6H_3\end{matrix}\right.\left\{\begin{matrix}(1)OH\\(2)CO_2Na\end{matrix}\right.$	From salicylic acid.
Tolylene Orange G.	$\begin{matrix}C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(4)C_6H_2\end{matrix}\right.\\ \\ C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(4)C_6H\end{matrix}\right.\end{matrix}\left\{\begin{matrix}(6)CH_3\\(1)OH\\(2)CO_2Na\\(5)SO_3Na\\(1)NH_2\\(3)NH_2\\(6)CH_3\end{matrix}\right.$	From cresotic acid.
Tolylene Orange R.	$\begin{matrix}C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(4)C_6H\end{matrix}\right.\\ \\ C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(4)C_6H\end{matrix}\right.\end{matrix}\left\{\begin{matrix}(6)CH_3\\(1)NH_2\\(3)NH_2\\(5)SO_3Na\\(6)CH_3\\(1)NH_2\\(3)NH_2\\(5)SO_3Na\end{matrix}\right.$	....
Rosazurin G.	$C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(1)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(2)NHC_2H_5\\(7)SO_3Na\end{matrix}\right.$ $C_6H_3\left\{\begin{matrix}(3)CH_3\\N=N-(1)C_{10}H_5\end{matrix}\right.\left\{\begin{matrix}(2)NH_2\\(7)SO_3Na\end{matrix}\right.$	From δ acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown paste; insoluble in water.	Orange solution.	....	Green.	....	Slightly soluble in alcohol. Chrome dye for wool.
Brown powder; brown solution.	Brown ppt.	Brown ppt.	Violet.	Brown ppt.	Direct dye for cotton.
Brown powder; yellow solution.	Brown.	Brown ppt.	Red.	Brown ppt.	Soluble in alcohol.
Red powder; red solution.	Red ppt.	Blue ppt.	Blue.	Blue ppt.	Soluble in alcohol.
Yellow powder; yellow solution.	Orange ppt.	Green ppt.	Violet.	Brown ppt.	Soluble in alcohol.
Brown powder; yellow solution.	Brown.	Brown ppt.	Violet.	Brown ppt.	Brown ppt. with acetic acid.
Orange powder; yellow solution.	Redder.	Brown ppt.	Red.	Brown ppt.	....
Red powder; orange solution.	No change.	Violet ppt.	Brown.	Red ppt.	....
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	....

Commercial name	Formula	Remarks
Rosazurin B.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NHC_2H_5\\(7)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NHC_2H_5\\(7)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From δ acid.
Diamine Red 3 B. Deltapurpurin 7 B.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\(7)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\(7)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From δ acid.
Brilliant Purpurin.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From naphthionic and R acids.
Congo Orange R.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(3)SO_3Na\\(6)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(1)C_6H_4(4)OC_2H_5\end{array}\right.\end{array}$	From R acid and phenol.
Azo Mauve.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-C_{10}H_3\left\{\begin{array}{l}NH_2\\OH\\(SO_3Na)_2\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-C_{10}H_6.NH_2\end{array}\right.\end{array}$	....
Cotton Red.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(2)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH\cdot\\(4)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From naphthionic acid.
Azo Blue.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From N W acid.
Congo Corinth B.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From N W acid.
Benzopurpurin 4 B. Eclipse Red. Imperial Red. Victoria Red.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From naphthionic acid.
Benzopurpurin 6 B.	$\begin{array}{l}C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(5)SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\C_6H_3\left\{\begin{array}{l}(3)CH_3\\N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(5)SO_3Na\end{array}\right.\end{array}\right.\end{array}$	From L acid.

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	....
Brown powder; red solution in hot water.	Red ppt.	Brown ppt.	Blue.	Brown ppt.	Violet ppt. with acetic aid. Precipitated by magenta.
Red powder; red solution.	Red ppt.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol.
Orange powder; orange solution.	No change.	Brown ppt.	Blue.	Brown ppt.	Soluble in alcohol.
Black powder; violet solution.	No change.	Violet ppt.	Blue.	Violet.	....
Red powder; red solution.	No change.	Blue ppt.	Blue.	Blue ppt.	....
Black powder; violet solution.	Red.	Violet ppt.	Blue.	Violet ppt.	....
Black powder; red solution.	Cherry-red.	Violet ppt.	Blue.	Violet ppt.	Bluer solution with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Blue ppt.	Blue.	Blue ppt.	Brown ppt. with acetic acid.
Red powder; orange solution.	Red.	Blue ppt.	Blue.	Blue ppt.	Blue ppt. with acetic acid.

Commercial name	Formula	Remarks
Benzopurpurin B.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\ (6)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\ (6)SO_3Na\end{array}\right.\end{array}\right.$	From Br acid.
Deltapurpurin 5 B.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\ (6)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\ (7)SO_3Na\end{array}\right.\end{array}\right.$	From δ and Br acids.
Brilliant Congo R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(1)C_{10}H_5\left\{\begin{array}{l}(2)NH_2\\ (6)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(1)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\ (3)SO_3Na\\ (6)SO_3Na\end{array}\right.\end{array}\right.$	From Br and R acids.
Congo Red 4 R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\ (4)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(4)C_6H_3\left\{\begin{array}{l}(1)OH\\ (3)OH\end{array}\right.\end{array}\right.$	From naphthionic acid and resorcinol.
Diamine Blue 3 B.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-C_{10}H_3\left\{\begin{array}{l}(1)NH_2\\ (8)OH\\ (3)SO_3Na\\ (6)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-C_{10}H_3\left\{\begin{array}{l}(1)NH_2\\ (8)OH\\ (3)SO_3Na\\ (6)SO_3Na\end{array}\right.\end{array}\right.$	From H acid.
Diamine Blue B X.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\ (4)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(2)C_{10}H_3\left\{\begin{array}{l}(1)NH_2\\ (8)OH\\ (3)SO_3Na\\ (6)SO_3Na\end{array}\right.\end{array}\right.$	From N W and H acids.
Hessian Brown M M.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(2)C_6H_2\left\{\begin{array}{l}(1)OH\\ (3)OH\\ (4)N=N-(1)C_6H_4(4)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(2)C_6H_2\left\{\begin{array}{l}(1)OH\\ (3)OH\\ (4)N=N-(1)C_6H_4(4)SO_3Na\end{array}\right.\end{array}\right.$	From Resorcin Yellow.
Benzo Black Blue R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(4)C_{10}H_6(1)N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\ (4)SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\ (4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Direct Grey B.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-C_{10}H_3\left\{\begin{array}{l}(OH)_2\\ CO_2Na\\ SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-C_{10}H_3\left\{\begin{array}{l}(OH)_2\\ CO_2Na\\ SO_3Na\end{array}\right.\end{array}\right.$	....
Direct Blue R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-C_{10}H_3\left\{\begin{array}{l}(OH)_2\\ CO_2Na\\ SO_3Na\end{array}\right.\end{array}\right.$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N=N-C_{10}H_5\left\{\begin{array}{l}OH\\ SO_3Na\end{array}\right.\end{array}\right.$	....

Character of dyestuff	Reaction of aqueous solution.		Reaction of dye with sulphuric acid		Other characteristics.
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; brown solution.	No change.	Brown ppt.	Blue.	Brown ppt.	Brown solution with acetic acid-
Brown powder; orange solution.	Red ppt.	Brown ppt.	Blue.	Brown ppt.	Brown solution with acetic acid. $MgSO_4$ ppts. the diamine red present.
Brown powder; red solution.	Orange ppt.	Brown ppt.	Blue.	Black ppt.	Bluer solution with acetic acid. Precipitated by magenta.
Brown powder; red solution.	No change.	Violet ppt.	Blue.	Violet ppt.	Brown ppt. with acetic acid.
Grey powder; violet solution.	No change.	Violet ppt.	Blue.	Violet ppt.	....
Blue powder; violet solution.	Redder.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol.
Brown powder; brown solution.	Redder.	Brown ppt.	Black.	Brown ppt.	Soluble in alcohol.
Black powder; violet solution.	Blue ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol.
Black powder; violet solution in hot water.	Redder.	Grey ppt.	Blue.	Grey ppt.	Shades are fast to light.
Black powder; violet solution.	Redder.	Violet ppt.	Blue.	....	....

Commercial name	Formula	Remarks
Azo Black Blue.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-(2)C_{10}H_3\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(6)SO_3Na\\(8)NH_2\end{array}\right.\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-(1)C_6H_3\left\{\begin{array}{l}(2)NH.C_6H_5\\(4)OH\end{array}\right.\end{array}\right.$	....
Oxamine Blue 3 R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-(2)C_{10}H_4\left\{\begin{array}{l}(1)OH\\(3)SO_3Na\\(6)NH_2\end{array}\right.\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-(2)C_{10}H_5\left\{\begin{array}{l}(1)OH\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From N W acid.
Azo Corinth.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_2\left\{\begin{array}{l}N{=}N-C_{10}H_6.SO_3Na\\OH\\OH\end{array}\right.\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_2\left\{\begin{array}{l}OH\\NH_2\\SO_3Na\end{array}\right.\end{array}\right.$	From naphthionic acid.
Pyramidol Brown.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_3(ONa)_2(2.4)\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_3(ONa)_2(2.4)\end{array}\right.$	From resorcinol.
Azo Orange R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_{10}H_5\left\{\begin{array}{l}NH_2\\SO_3Na\end{array}\right.\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_3OH\end{array}\right.\Big\}CH_2$ $C_6H_3\left\{\begin{array}{l}N{=}N-C_6H_3OH\\(3)CH_3\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_{10}H_5\left\{\begin{array}{l}NH_2\\SO_3Na\end{array}\right.\end{array}\right.$	From naphthionic acid.
Mekong Yellow R.	$C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_3\left\{\begin{array}{l}OH\\CO_2Na\end{array}\right.\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_3OH\end{array}\right.\Big\}CH_2$ $C_6H_3\left\{\begin{array}{l}N{=}N-C_6H_3OH\\(3)CH_3\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)CH_3\\ N{=}N-C_6H_3\left\{\begin{array}{l}OH\\CO_2Na\end{array}\right.\end{array}\right.$	From salicylic acid.
From di-o-chlor-benzidine. Dianol Red 2 B.	$C_6H_3\left\{\begin{array}{l}(3)Cl\\ N{=}N(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.$ $\vert$ $C_6H_3\left\{\begin{array}{l}(3)Cl\\ N{=}N(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.\end{array}\right.$	From naphthionic acid.
From Diamino-stilbene. Stilbene Red.	$CH.C_6H_4-N{=}N-(1)C_{10}H_4\left\{\begin{array}{l}(2)NH_2\\(SO_3Na)_2\end{array}\right.$ $\Vert$ $CH.C_6H_4-N{=}N-(2)C_{10}H_5\left\{\begin{array}{l}(1)NH_2\\(4)SO_3Na\end{array}\right.$	From naphthionic acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; violet solution.	....	Violet ppt.	Blue.	Violet ppt.	Direct dye for cotton.
Violet powder; violet solution.	Violet ppt.	Violet ppt.	Blue.	Violet ppt.	Soluble in alcohol. Direct dye for cotton.
Brown powder; brown solution.	Violet.	Brown ppt.	Violet.	Brown ppt.	Direct dye for cotton.
Dark brown powder; reddish-brown solution.	Brownish-red.	Brown ppt.	Violet solution.	Brown-black ppt.	Direct cotton dyestuff.
Red powder; orange solution.	Redder.	Grey ppt.	Blue.	Grey ppt.	Direct dye for cotton.
Brown powder; brown solution.	Redder.	Brown ppt.	Violet.	Brown ppt.	Direct dye for cotton.
Brownish-red powder: red solution.	Red solution.	Violet solution.	Blue.	Violet.	Direct dye for cotton.
Brown powder; red solution.	No change.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol.

Commercial name	Formula	Remarks
Brilliant Yellow.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_6H_4(4)OH \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_6H_4(4)OH \end{matrix} \right. \end{matrix}$	From phenol.
Polychromin B.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_6H_4(4)NH_2 \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_6H_4(4)NH_2 \end{matrix} \right. \end{matrix}$	....
Chrysophenin.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(4)C_6H_4(1)OC_2H_5 \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(4)C_6H_4(1)OC_2H_5 \end{matrix} \right. \end{matrix}$	From Brilliant Yellow.
Hessian Purple N.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_6(2)NH_2 \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_6(2)NH_2 \end{matrix} \right. \end{matrix}$	....
Brilliant Hessian Purple.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \left\{ \begin{matrix} (2)NH_2 \\ (6)SO_3Na \end{matrix} \right. \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \left\{ \begin{matrix} (2)NH_2 \\ (6)SO_3Na \end{matrix} \right. \end{matrix} \right. \end{matrix}$	....
Hessian Purple B.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \left\{ \begin{matrix} (2)NH_2 \\ SO_3Na \end{matrix} \right. \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \left\{ \begin{matrix} (2)NH_2 \\ SO_3Na \end{matrix} \right. \end{matrix} \right. \end{matrix}$	From β acid.
Hessian Purple D.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \left\{ \begin{matrix} (2)NH_2 \\ SO_3Na \end{matrix} \right. \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_5 \left\{ \begin{matrix} (2)NH_2 \\ SO_3Na \end{matrix} \right. \end{matrix} \right. \end{matrix}$	From γ acid.
Hessian Yellow.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-C_6H_3 \left\{ \begin{matrix} (1)OH \\ (2)CO_2H \end{matrix} \right. \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-C_6H_3 \left\{ \begin{matrix} (1)OH \\ (2)CO_2H \end{matrix} \right. \end{matrix} \right. \end{matrix}$	From salicylic acid.
Hessian Violet.	$\begin{matrix} CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(4)C_{10}H_6(1)NH_2 \end{matrix} \right. \\ \Vert \\ CH.C_6H_3 \left\{ \begin{matrix} (2)SO_3Na \\ N=N-(1)C_{10}H_6(2)OH \end{matrix} \right. \end{matrix}$	....
Diamino-azoxy derivatives. St. Denis Red.	$O \left\langle \begin{matrix} N-C_6H_3 \left\{ \begin{matrix} CH_3 \\ N=N-C_{10}H_5 \left\{ \begin{matrix} OH \\ SO_3Na \end{matrix} \right. \end{matrix} \right. \\ \vert \\ N-C_6H_3 \left\{ \begin{matrix} CH_3 \\ N=N-C_{10}H_5 \left\{ \begin{matrix} OH \\ SO_3Na \end{matrix} \right. \end{matrix} \right. \end{matrix} \right.$	From N W acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder; orange solution.	Redder.	Violet ppt.	Violet.	Violet ppt.	Precipitated by magenta.
Brown powder; orange solution.	No change.	Black ppt.	Violet.	Black ppt.	Yields ingrain colours.
Orange powder; orange solution.	Yellow.	Brown ppt.	Violet.	Blue ppt.	....
Red powder; red solution.	Red ppt.	Black ppt.	Blue.	Black ppt.	Violet ppt. with acetic acid. Precipitated by magenta.
Red powder; red solution.	Red ppt.	Black ppt.	Blue.	Black ppt.	Soluble in alcohol.
Brown powder; red solution.	Violet ppt.	Black ppt.	Violet.	Brown ppt.	....
Black powder; orange solution.	Bluer.	Brown ppt.	Violet.	Brown.	....
Yellow powder; yellow solution.	Red.	Black ppt.	Violet.	Black ppt.	....
Black powder; violet solution.	Bluer.	Blue ppt.	Blue.	Violet ppt.	....
Red powder; red solution.	Red ppt.	Red ppt.	Red.	Red ppt.	Soluble in alcohol.

Commercial name	Formula	Remarks.
Acid Milling Scarlet.	$O\left\langle\begin{matrix} N-C_6H_3\begin{cases}CH_3\\ N=N-(2)C_{10}H_5\begin{cases}(1)OH\\ (4)SO_3Na\end{cases}\end{cases}\\ N-C_6H_3\begin{cases}CH_3\\ N=N-(1)C_{10}H_4\begin{cases}(2)OH\\ (3)SO_3Na\\ (6)SO_3Na\end{cases}\end{cases}\end{matrix}\right.$	From R acid.
Rock Scarlet Y S.	$O\left\langle\begin{matrix} N-C_6H_3\begin{cases}CH_3\\ N=N-(2)C_{10}H_5\begin{cases}(1)OH\\ (4)SO_3Na\end{cases}\end{cases}\\ N-C_6H_3\begin{cases}CH_3\\ N=N-(1)C_{10}H_6(2)OH\end{cases}\end{matrix}\right.$	From N W acid.
From amino-acetanilide. Salmon Red.	$OC\left\langle\begin{matrix} NH.C_6H_4-N=N-C_{10}H_5\begin{cases}(1)NH_2\\ (4)SO_3Na\end{cases}\\ NH.C_6H_4-N=N-C_{10}H_5\begin{cases}(1)NH_2\\ (4)SO_3Na\end{cases}\end{matrix}\right.$	From naphthionic acid.
Cotton Yellow G.	$OC\left\langle\begin{matrix} NH.C_6H_4-N=N-C_6H_3\begin{cases}(1)OH\\ (2)CO_2Na\end{cases}\\ NH.C_6H_4-N=N-C_6H_3\begin{cases}(1)OH\\ (2)CO_2Na\end{cases}\end{matrix}\right.$	From salicylic acid.
Cotton Scarlet.	$CH\begin{cases}C_6H_2(CH_3)_2-N=N-C_{10}H_4\begin{cases}OH\\ (SO_3Na)_2\end{cases}\\ C_6H_5\\ C_6H_2(CH_3)_2-N=N-C_{10}H_4\begin{cases}OH\\ (SO_3Na)_2\end{cases}\end{cases}$	From R acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Red powder; red solution.	Orange ppt.	No change.	Red.	Scarlet.	Shades are fast to milling.
Red powder; red solution.	Orange ppt.	Scarlet ppt.	Violet.	Scarlet ppt.	Shades are fast to milling.
Brown powder; orange solution.	No change.	Violet ppt.	Red.	Violet ppt.	....
Yellow powder; yellow solution.	Orange.	Brown ppt.	Orange.	Violet ppt.	....
Brown powder; red solution.	Redder.	No change.	Red.	Orange.	....

Benzopurpurin B is isomeric with the last-named dye, and is prepared by the reaction of diazotised tolidine on β-naphthylaminesulphonic acid in presence of alkali. It dyes cotton a colour approaching a turkey-red in shade and brilliancy. Acids turn the dyed fibre blue, the colour being restored by alkalies or washing.

Chrysophenin.—This forms a light orange powder, partially soluble in water. The solution is unchanged by alkalies, but gives a dark brownish-red precipitate with acids. In a neutral bath it dyes both wool and cotton a bright yellow, unaffected by dilute acids, alkalies, or soaps.

INGRAIN COLOURS (ICE COLOURS. DEVELOPED COLOURS).

An especially fast class of dyeings on cotton are obtained by the production of azo-dyestuffs in the fibre itself by the interaction of solutions containing their "components." This effect may be produced in two ways. By the first method a dyestuff is first dyed into the fabric and then diazotised in the fibre by immersion in a nitrous acid solution. The finished shade is then developed, after rinsing, by immersion in a solution of a suitable amine or phenol. As examples of dyestuffs which are frequently diazotised and developed in the fibre in this manner may be mentioned diamine black, the diaminogen colours, and primuline. As developers solutions of β-naphthol, α-naphthylamine or *m*-phenylenediamine are commonly used, but other naphthols, naphthylamines, diamines and aminonaphthol ethers, and also resorcinol, are used for this purpose. By the other method the fibre is first padded with an alkaline solution of a phenol, usually of β-naphthol; this substance apparently is closely fixed by the cotton fibre. The fabric is then immersed in a solution of a diazo-compound, neutralised with sodium acetate or chalk. Most usually, diazotised *p*-nitraniline is used and forms on the fibre the brilliant and very fast red shade known as paranitraniline red (*p*-nitrobenzene-azo-β-naphtol); but the diazo-derivatives of *m*-nitraniline, the naphthylamines, and aminoazobenzene are also occasionally employed. Many preparations are now sold which obviate the necessity of diazotising the *p*-nitraniline in the dye-works; one of these, Nitrosamine Red, has already been described (page 122). Others consist of intimate mixtures of diazo-*p*-nitraniline with metallic salts containing water of crystallisation, such as alum and

sodium sulphate, which counteract the explosive properties of the diazo-compounds.

Azophor Red and Nitrazol are preparations of this class, the former containing aluminium sulphate. The strength of these preparations is ascertained by dissolving in ice-cold water and running the solution into an alkaline solution of β-naphthol of known strength until the diazo-compound is present in slight excess as shown by spotting on paper, and allowing the outer ring of clear liquid to react with an alkaline solution of R-salt (α-naphtholdisulphonic acid). When excess of diazo-compound is present a red colouration will appear. 144 parts by weight of β-naphthol are equivalent to 185.5 parts of *p*-nitrodiazobenzenechloride.

General Analytical Reactions of Azo-dyes.

The great majority of the azo-dyes are sulphonated, and more or less soluble in water. In no case is a sulphonated dye removed from its aqueous solution by agitation with ether, whether the liquid be alkaline or acid. There are a limited number of unsulphonated azo-dyes, such as *Chrysoïdine* and *Bismarck Brown*, from which the free base may be extracted by agitating the alkaline solution with ether. *Chrysamin*, on the other hand, is an unsulphonated azo-dye of acid character, and is removed from its acidified aqueous solution on agitation with ether.

The azo-dyes are stated to be non-poisonous. Out of those which have been examined, only 2 have proved to be poisonous in a slight degree, namely: Metanil Yellow and Orange II. On addition of hydrochloric acid to the concentrated aqueous solution of a hydroxyazo-dye, a precipitate is usually produced if the colouring matter contain only 1 SO_3H group, as in that case the free sulphonic acid often is insoluble or sparingly soluble in water. But when the free acid contains 2 sulphonic groups it is soluble in water, and hence is not precipitated when the solution of the dye is acidified. Tropæolin OOO gives a purple precipitate soluble in excess of hydrochloric acid, and some of the scarlets behave similarly.

The alkali hydroxides and ammonia do not usually produce a precipitate in solutions of the sulphonated azo-dyes; but they often change the colour, owing to the replacement of the hydrogen of the hydroxyl groups.

The concentrated solutions of many of the azo-dyes are precipitated

by barium and calcium chlorides, and in some cases the reactions are of analytical interest. The azo-dyes as a class are remarkable for the striking colourations produced when the solid substance is treated with concentrated sulphuric acid, as was first pointed out by J. Spiller (*Chem. News*, 1880, **42**, 191). To apply the test it is merely necessary to heat a few grains of the solid substance in a test-tube or porcelain crucible with strong sulphuric acid. Very frequently, useful information can be gained by observing the spectrum of the coloured liquid obtained. In the case of the tetrazo-dyes the colour of the solution in strong sulphuric acid is an important indication of the constitution of the colouring matter.

Among the most characteristic reactions of the azo-dyes is their behaviour with reducing agents, the most generally suitable reagent for the purpose being hydrochloric acid and zinc or solution or stannous chloride or an acid solution of titanous chloride or sulphate. Thus the amino-azo-compounds are split up into a primary amine and para-diamine, amino-azobenzene yielding aniline and paraphenylene-diamine (para-diamino-benzene) – $C_6H_5N : N . C_6H_4 . NH_2 + 2H_2 = C_6H_5.NH_2 + C_6H_4(NH_2)_2$. (See Witt, *Ber.*, 1888, **21**, 3471 and 1886, **19**, 1721).

An acid solution of stannous chloride reduces the hydroxyazo-dyes in a similar manner, the products being a primary amine and an aminophenol. Thus hydroxyazobenzene yields aniline, $C_6H_5NH_2$, and *p*-aminophenol, $C_6H_4(NH_2)OH$. Mandarin splits up similarly into sulphanilic acid, $C_6H_5(SO_3H)NH_2$, and amino-β-naphthol, $C_{10}H_6(NH_2)OH$. When the naphthol group is sulphonated, the aminonaphthol-sulphonic acid decomposes into amino-naphthol and free sulphuric acid. Thus Xylidine-Red is decomposed as follows: $C_6H_3(CH_3)_2N:N:C_{10}H_4.(SO_3Na)_2OH + 2H_2O = C_6H_3(CH_3)_2NH_2 + C_{10}H_6(NH_2).OH + 2NaHSO_4$. With an alkaline reducing agent, such as ammonium sulphide or zinc and ammonia, the aminonaphthol-disulphonic acid does not undergo decomposition.

Secondary azo-dyes split up in a similar manner under the action of reducing agents. Thus with metallic tin or stannous chloride and hydrochloric acid, Biebrich Scarlet yields sulphanilic acid, paradiamino-benzene, and aminonaphthol. With an alkaline reducing agent, such as zinc and ammonia, Biebrich Scarlet undergoes a modified decomposition, resulting in the formation of aminohydrazo-benzenesulphonate and amino-naphthol,

On exposing the decolourised liquid to the air it rapidly acquires a yellow colour, from the production of sodium amino-azo-benzene-sulphonate. Other tetrazo-dyes behave similarly.

Congo-Red, the type of the benzidine dyes, on reduction yields benzidine and a diaminonaphthalene-sulphonic acid, $C_{10}H_5(SO_3H)\alpha(NH_2)\alpha(NH_2)\beta$.

It will be seen that the investigation of the behaviour of the azo-dyes with reducing agents affords a most valuable means of recognizing them and ascertaining their constitution. The bases resulting from the treatment can be extracted from the alkaline liquid with ether, and if more than one be produced they can be separated by fractional distillation or crystallisation of their salts. The isolation and identification of the aminophenols is very difficult, especially as some of them are very readily affected by air. Hence it is preferable, when it is desired to obtain them in a pure state, to evaporate the neutralised solution to dryness, and heat the residue with anhydrous sodium carbonate.

The following table gives some of the leading characters of certain of the bases produced by the reduction of commercial azo-dyes:

Name	Formula	M. p.	B. p.	Other characters
Aniline. Aminobenzene. Phenylamine.	$C_6H_5.NH_2$	-8°	183.7°	Sparingly soluble. Violet colour with bleaching powder solution.
o-Toluidine. *o*-Aminotoluene.	$C_6H_4\left\{\begin{matrix}(1)CH_3\\(2)NH_2\end{matrix}\right.$	Below -20°	198°	Brown colour with bleaching powder solution. Colour soluble in ether, and changed to pink by dilute acetic acid.
p-Toluidine. Paraminotoluene.	$C_6H_4\left\{\begin{matrix}(1)CH_3\\(4)NH_2\end{matrix}\right.$	45°	198°	White, crystalline. No reaction with bleaching powder. Dissolved in strong H_2SO_4 and nitric acid added, gives blue, changing to red.
α-Naphthylamine. α-Aminonaphthalene.	$C_{10}H_7.NH_2$	50°	300°	Characteristic and persistent odour. Turns violet on exposure. $FeCl_3$ and other oxidising agents give azure-blue precipitate.
Diphenylamine.	$(C_6H_5)_2.NH$	54°	110°	Nearly insoluble plates. Deep blue colour on adding to its solution in pure sulphuric acid a trace of nitrous sulphuric acid.
p-Amino-diphenylamine.	$NH_2.C_6H_4.-NH.C_6H_5$	61°	......	Small lustrous plates, becoming green in the air. $FeCl_3$ gives a red colour, changing to green, and on concentration a green precipitate, soluble in H_2SO_4 with a carmine-red colour.

Name	Formula	M. p.	B. p.	Other characters
p-Phenylene-diamine. *p*-Diamino-benzene.	$C_6H_4:(N_2H_2)$	140°	267°	Sparingly soluble tablets. Oxidised to quinone by MnO_2 and dilute H_2SO_4.
Dimethyl-*p*-diamino-benzene.	$C_6H_4:\left\{\begin{matrix}NH_2\\N(CH_3)_2\end{matrix}\right.$	41°	257°	Easily soluble. Gives methylene blue with a solution of H_2S in hydrochloric acid in presence of $FeCl_3$.
p-Amino-phenol.	$C_6H_4\left\{\begin{matrix}(1)OH\\(4)NH_2\end{matrix}\right.$	184° decomposing.	......	Colourless plates, rapidly turning brown. Alkaline solution becomes violet on exposure, and yields quinone with oxidising agents. With bleaching powder solution, a violet-colour, changing to green.
α-Amino-*α*-naphthol.	$C_{10}H_6\left\{\begin{matrix}(1)OH\\(8)NH_2\end{matrix}\right.$	....	......	On agitating the alkaline solution with air a dirty green colour is produced, changing to yellow. With bromine water, yellow-white crystalline precipitate. With oxidising agents yields the theoretical amount of *a*-naphthaquinone.
β-Amino-*α*-naphthol.	$C_{10}H_6\left\{\begin{matrix}(1)OH\\(2)NH_2\end{matrix}\right.$	....	......	On agitating the alkaline solution with air, permanent grass-green colour; and green scum soluble in alcohol to pure green solution. Br and $FeCl_3$ give yellowish or green precipitate, and no naphthaquinone is formed on heating.
Amino-resorcinol.	$C_6H_3(OH)_2.NH_2$	....	......	Flat plates turning green in the air. NaOH gives deep blue colour, changing to green and brown. $FeCl_3$ gives deep brown colour, and then nearly black precipitate.

5. Hydroxyketones.

The hydroxyketone colours are chiefly derivatives of anthracene.

Such of the hydroxy-derivatives of anthraquinone as receive practical application are not known generally by their systematic or descriptive names, but are simply termed "alizarin for reds," "alizarin for blues," etc. Hence it will be convenient to describe fully the characters of true alizarin, and subsequently treat of the various products known in commerce as "alizarin."

Alizarin. Ortho-dihydroxy-anthraquinone.

$$C_{14}H_8O_4 = C_6H_4 < \begin{matrix}CO\\CO\end{matrix} > C_6H_2\left\{\begin{matrix}(1)OH\\(2)OH\end{matrix}\right.$$

Alizarin exists ready-formed in madder-root (*Rubia tinctorum*), but the proportion of actual alizarin is, except in old roots, small compared

with that existing potentially in the form of ruberythric acid, a glucoside which on steeping the madder roots in water is resolved, under the influence of a peculiar ferment called erythrozyme, into alizarin and dextrose, according to the following equation:

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

Alizarin is manufactured artificially on a very large scale from anthracene. The synthesis of alizarin was first effected by Graebe and Leibermann, in 1868.

Alizarin crystallises from alcohol in reddish-yellow prisms or needles containing $3H_2O$, which it loses at 100°. It melts at 289°–299°[1] and sublimes at a somewhat higher temperature in magnificent orange-red needles.

Alizarin is nearly insoluble in cold water, and requires 3220 parts of boiling water for solution. Cold alcohol dissolves it but sparingly, but in boiling alcohol, glacial acetic acid, and glycerin it is more soluble. It is also readily soluble in ether, carbon disulphide, and benzene, and may be extracted by agitation with these solvents. In strong sulphuric acid, alizarin dissolves with dark brownish-red colour, and is precipitated unchanged on diluting the solution with water.

In solutions of alum and aluminium sulphate alizarin is almost insoluble, a character which distinguishes it from purpurin, which dissolves in boiling alum solution, forming a yellowish-red and strongly fluorescent liquid.

Alizarin has the characters of a weak acid. It dissolves in solutions of carbonates of the alkali-metals, apparently without decomposing them, and it also dissolves in a boiling solution of sodium acetate, separating again unchanged on cooling; but if the boiling be continued for some time, acetic acid is given off and sodium alizarate remains in solution. With alkali hydroxides it reacts to form true compounds or *alizarates*, the solutions of which are violet by transmitted, and purple by reflected, light. A solution of sodium alizarate gives insoluble, coloured precipitates or "lakes" with most metallic solutions. Thus with barium and calcium salts it yields purple precipitates (distinction from monohydroxyanthraquinone) which are soluble in water containing carbonic acid. With aluminium and tin, alizarin forms red lakes, and has such affinity for these metals that it is capable of decom-

[1] This is the m. p. of alizarin according to Claus and Wilgerodt. Schunck gives 282° as the m. p.

posing dilute solutions of nitrates or chlorides containing them. With ferric salts, sodium alizarate yields a black-violet precipitate, but with ferrous salts a violet precipitate is formed. An alcoholic solution of free alizarin also gives a purple precipitate with ferric chloride.

By heating in the solid state with zinc-dust, alizarin is reduced to anthracene, $C_{14}H_{10}$. If dissolved in weak sodium carbonate and treated in the cold with zinc-dust, the violet solution becomes red. When alizarin is boiled with zinc-dust and ammonia it is reduced to a body of the formula $C_{14}H_{10}O_3$, to which the name anthrarobin has been given.[1]

The solution of alizarin in ammonia or alkali carbonate differs from that of purpurin in being non-fluorescent, but exhibits a characteristic absorption-spectrum, having a well-defined band in the yellow, and another narrower one between the orange and red. There is also another faint band about E, scarcely distinguishable from the general absorption occurring in that region. The absorption spectra of the solutions of alizarin in ether and carbon disulphide are not characteristic. When boiled with acetic anhydride, alizarin yields a mono-acetal-derivative, and on prolonged boiling diacetyl-alizarin, $C_{14}H_6(O.C_2H_3)_2O_2$.

The methods of analysis of alizarin in its manufacture is discussed by Perkin (*J. S. D. and Col.* 1897, **13**, 81).

Alizarin-sulphonic Acid. $C_{14}H_5O_2(OH)_2(SO_3H)$. This substance is formed by heating alizarin with fuming sulphuric acid until the product is completely soluble in water. The liquidi s thendiluted, and the unaltered sulphuric acid precipitated by lime or baryta.

Alizarin-sulphonic acid is freely soluble in water and forms 3 series of salts, according to the number of hydrogen atoms replaced. The salts of the alkali-metals containing 1 atom of base are yellow or orange and soluble in water; those with 2 atoms are reddish-violet; and those with 3 atoms intensely violet.

Sodium alizarin-sulphonate, $C_{14}H_5O_2(OH)_2(SO_3Na)$, constitutes the colouring matter known in commerce as *Alizarin Carmine*, *Alizarin Powder W*, and *Alizarin WS* or *S*. It forms an orange-yellow powder, easily soluble in water or alcohol with orange or brownish-yellow colour. The solution is turned bright yellow by hydrochloric acid and violet by sodium hydroxide. In strong sulphuric acid the

[1] Commercial anthrarobin contains a trace of zinc, but the entire ash should not exceed 0.3 %.

dye dissolves with yellowish-red colour, changing to bright yellow on dilution. Alizarin Carmine dyes wool mordanted with alumina scarlet, while tin mordants give orange and chromium claret-red shades; but the colours are not so bright as those obtained with sulphonated azo-dyes.

β-Nitroalizarin. $C_6H_4:C_2O_2:C_6H(NO_2)(OH)_2$. By direct treatment with nitric acid, alizarin is converted into phthalic acid, $C_6H_4(COOH)_2$; but by the action of nitric acid on alizarin dissolved in glacial acetic acid or petroleum spirit, β-nitroalizarin is obtained. This body, which constitutes the *Alizarin Orange* of commerce, was formerly prepared by exposing cloth dyed with Alizarin Red to nitrous fumes, but is now directly obtained by treating alizarin in nitrobenzene solution with nitric acid of 30°–40° B. When pure, nitroalizarin forms yellow needles or leaflets, which melt at 244° and sublime at a higher temperature with partial decomposition. It is nearly insoluble in water, but dissolves in glacial acetic acid. The solution in sodium hydroxide is magenta-red, and on treatment with zinc-dust gradually becomes blue and then yellowish-brown, the indigo-blue colour returning on exposing the filtered liquid to the air. Other reactions of Alizarin Orange are given in the tables.

β-Nitroalizarin derives its chief practical interest from its reaction with glycerol and sulphuric acid,[1] whereby it is converted into dihydroxyanthraquinone-quinoline, or *Alizarin Blue*, according to the following equation:

$$C_6H_4:C_2O_2:C_6\left\{\begin{array}{l}(\alpha 1)OH\\(\beta 1)OH\\(\beta 2)H\\(\alpha 2)NO_2\end{array}\right. + \begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array} =$$

$$C_6H_4:C_2O_2:C_6\left\{\begin{array}{l}OH\\OH\\\left.\begin{array}{l}CH:CH.\\N\ :CH.\end{array}\right\}\end{array}\right. +O_2+3OH_2.$$

Alizarin Blue, $C_{17}H_9NO_4$. In the pure state it forms dark blue or brownish-violet needles, m. p. 270°, and may be partially sublimed without decomposition. In commerce, Alizarin Blue occurs as minute

[1] 1 part of nitroalizarin in fine powder is heated with 5 parts of strong sulphuric acid and 5 of absolute glycerine to 150°. When the reaction is completed, the product is boiled with excess of water, when the colouring matter dissolves, but is deposited on cooling as a flocculent brown precipitate. When this is washed with water, it loses sulphuric acid and becomes blue.

shining crystals, or as a dark violet paste containing 10% of the dry substance. The pure colouring matter can be obtained by boiling the dried paste with glacial acetic acid, the Alizarin Blue being deposited in crystals on cooling. It is insoluble in water, but dissolves with blue colour in hot alcohol, and is sparingly soluble in benzene.

Alizarin Blue exhibits both acid and basic characters, a property doubtless due to the simultaneous presence of OH groups and a pyridine residue in the molecule. With dilute sulphuric acid Alizarin Blue unites to form a brown compound, which is decomposed by washing with water. In strong sulphuric acid it dissolves with red, and in phosphoric and arsenic acids with reddish-yellow colour.

In dilute alkali hydroxides Alizarin Blue dissolves with greenish-blue colour, but the solution is precipitated by excess of alkali. By treating the solution of Alizarin Blue in alkali hydroxide with metallic solutions a series of insoluble lakes may be obtained. The compounds with lime, baryta, and ferric oxide are greenish-blue, that with nickel oxide blue, and those with alumina and oxide of chrominum bluish-violet.

When treated with zinc-dust in alkaline solution, Alizarin Blue is reduced giving a red colouration, but the blue colour returns on exposing the filtered liquid to the air. Other reducing agents may be employed, and the property may be applied for the production of an Alizarin Blue vat, similar to that used in indigo-dyeing. Alizarin Blue is too expensive to be used generally as a substitute for indigo, and its tendency to form insoluble lakes is not in its favour. The colour is not so fast to light as indigo, but is less readily attacked by oxidising agents, such as hypochlorites, chromic acid, and alkaline solutions of ferricyanides.

The inconvenience attending the employment of ordinary Alizarin Blue can be overcome by converting it into a soluble form, by treating the commercial paste with a concentrated solution of sodium hydrogen sulphite. After standing ten days or a fortnight, the liquid is filtered, and the new colouring matter obtained in the solid state by evaporation at a low temperature or salting out.

Alizarin blue S, or *Soluble Alizarin Blue*, obtained as above described, is the sodium bisulphite compound of dihydroxyanthraquinone-quinoline. It occurs in commerce as a dark purple or chocolate-brown powder, which dissolves easily in water with yellowish-brown colour. In strong sulphuric acid the solid dye dissolves with deep yellow colour, and on dilution with water the

liquid yields a brownish precipitate. Dilute hydrochloric acid changes the colour of the aqueous solution to reddish-yellow, and soda turns it to bluish-violet. With excess of a strong acid or alkali, the bisulphite compound is decomposed with precipitation of the blue; but the solution is unaffected by salts of calcium, magnesium, or chromium, or by acetic or tartaric acid. On heating the aqueous solution above 70°, the bisulphite compound is decomposed, and the insoluble blue colouring matter is precipitated. This action is extensively applied in practice, and the colour produced being less affected by light than that given by insoluble Alizarin Blue, the soluble variety has almost superseded the older colouring matter both in printing and dyeing.

On the fibre, Alizarin Blue is unchanged by soap, soda, or solution of bleaching powder. When dyed on wool with a chrome mordant, nitric acid produces an orange colour, but otherwise the colour is discharged. Dilute hydrochloric acid turns the colour to violet, and sodium hydroxide to bluish-green, while an acid solution of stannous chloride changes the colour to a brownish-yellow. When treated with phosphoric acid of 1.435 sp. gr., Alizarin Blue is dissolved from the fibre with orange colour, and the solution, after dilution with water, is turned blue on adding ammonia. The absorption-spectrum of Alizarin Blue is characteristic, and the fact may be utilised for its detection.

Trihydroxyanthraquinones. $C_{14}H_5O_2(OH)_3$.

Of the 5 known compounds of this constitution 4 have a practical interest as colouring matters, and are described below. Of hydroxychrysazin, the fifth discovered isomer, very little is known.

Anthragallol $C_{14}H_8O_5$ forms the essential constituent of the colouring matter known as *Anthracene Brown*. It occurs as a dark brown paste inaoluble in water, but dissolving in alcohol with yellow colour.

Purpurin crystallises from its solution in hot alcohol in yellowish-red needles or prisms, containing $C_{14}H_5(OH)_3O_2 + H_2O$. It begins to sublime at 150°, m. p. 153°,but is more readily decomposed by heat than is alizarin. In water, purpurin is more soluble than alizarin, and the solution in hot water free from alkali has a yellow colour. Purpurin salso dissolves in alcohol and ether.

In alkali hydroxides, purpurin dissolves easily with a magenta or purple-red colour. It forms a compound with sodium hydroxide,

which crystallises in well-defined long prisms. The alkaline solutions of purpurin become decolourised on prolonged exposure to light. On strongly acidifying a solution of purpurin in an alkali with hydrochloric acid, purpurin hydrate is thrown down. The artificial purpurin paste probably consists chiefly of this body. When heated, it loses its water of hydration, and changes into ordinary purpurin. In warm alcohol it dissolves more readily than ordinary purpurin.

When heated with aqueous ammonia under pressure, purpurin is converted into purpurinamide, $C_{14}H_5(NH_2)(OH)_2O_2$. Owing to the formation of this compound, an ammoniacal solution of purpurin, if kept for several weeks, loses its power of dyeing mordanted cloth. On neutralising the solution, the purpurinamide forms a dark crystalline precipitate, soluble in alcohol or a large quantity of hot water, but separating again on cooling in long crimson needles, which exhibit a deep green metallic reflection. It dissolves freely in fuming nitric acid (sp. gr. 1.5) at the temperature of boiling water, and on cooling the solution deposits magnificent scarlet crystals, which are insoluble in water, ether, and carbon disulphide, and only slightly soluble in alcohol.

With acetic anhydride, purpurin forms a triacetyl derivative of the composition $C_{14}H_5(OC_2H_3O)_3O_2$, which crystallises in yellowish needles, m. p. 190°–193°. An alcoholic solution of purpurin gives with alcoholic lead acetate a dark crimson precipitate, which dissolves on treatment with an excess of the reagent to form a fine crimson solution, the spectrum of which shows three absorption-bands. Alizarin when similarly treated gives a purple colouration or precipitate.

An alcoholic solution of purpurin gives with alcoholic copper acetate a dark reddish-yellow precipitate, whereas alizarin, if pure, gives a purple solution, but no precipitate, when treated similarly.

With lime and baryta water purpurin yields purple-red precipitates and dyes cloth mordanted with alumina a colour varying from scarlet to dark red, without any shade of blue. Purpurin dyes cotton mordanted with ferric salts purple or black.

The most characteristic reaction of purpurin is its property of dissolving in a hot solution of alum with a reddish-yellow colour and greenish-yellow fluorescence. The purpurin-alumina lake behaves similarly. The fluorescence is seen to perfection in a liquid prepared by adding a solution of purpurin in sodium carbonate to one of alum

which has been previously treated with tartaric acid and sodium carbonate in quantity sufficient to prevent precipitation.

The absorption-spectrum of purpurin is characteristic. A solution of purpurin in alum or alkaline carbonate, if of suitable strength, gives 2 well-defined absorption-bands in the green, the less refrangible—situated about twice as far from line D as from line E[1]—being particularly sharp and black. The absorption-spectrum of the solution of purpurin in carbon disulphide contains 4 nearly equidistant absorption-bands, of which the first, which is somewhat more refrangible than the D line, is the narrowest, the second and third broader, but very distinct, while the fourth is scarcely distinguishable from the general absorption. An ethereal solution of purpurin is faintly fluorescent and shows a very dark narrow absorption-band slightly more refrangible than E, and a second wider and less defined band at F.

The detection of alizarin by a similar method is far less delicate, since alum cannot be used to separate it from the accompanying impurities, some of which produce absorption in that part of the spectrum in which all but the least refrangible of the absorption-bands occur, and this band is not the most intense or characteristic of those produced by alizarin (Stokes, *J. Chem. Soc.*, 1860, **12**, 219).

To detect small quantities of alizarin in purpurin, a solution of the colouring matter in sodium hydroxide should be exposed to the light till all the purpurin is destroyed. The liquid is then treated with dilute sulphuric acid and agitated with ether, alizarin being subsequently sought for in the evaporated ethereal solution.

Anthrapurpurin, Flavopurpurin. $C_6H_3(OH):C_2O_2:C_6H_2(OH)_2$ (see also page 218). These 2 isomeric compounds differ from each other and from purpurin simply in the position occupied in the molecule by the hydroxyl groups. They are produced by fusing β-anthraquinonedisulphonic acid and α-anthraquinonedisulphonic acid, respectively, with sodium hydroxide and potassium chlorate. Both are valuable colouring matters, and exist in various brands of commercial alizarin. Anthrapurpurin is as important a colouring matter as alizarin itself, and used with it increases its brilliancy, while alone it gives very brilliant scarlet shades. *Alizarin for reds* consist chiefly of anthrapurpurin, while flavopurpurin gives yellower shades. Both colouring matters present a close resemblance to alizarin, and the general reac-

[1] According to H. Morton, the refrangibility of the absorption-bands of a solution of purpurin in alum is sensibly affected by the temperature of the solution and the proportion of alum contained in it.

tions of the commercial pastes are shown in the tables. In the following table, the principal distinctions between anthra- and flavopurpurin are exhibited:

	Anthrapurpurin	Flavopurpurin
Positions of the OH groups.	1 : 2 : 7	1 : 2 : 6
Appearance.	Orange needles; anhydrous.	Golden-yellow needles; anhydrous.
Solubility in alcohol.	Easily soluble in boiling alcohol.	Easily soluble even in cold alcohol.
Solubility in hot benzene.	Almost insoluble.	Soluble.
Solubility in boiling water.	Slight; solution turns red on prolonged boiling.	Slight; solution remains yellow after prolonged boiling.
Solubility in solution of alum.	Slightly soluble with orange colour on boiling; separates again on cooling.	Insoluble.
Colour of solution in strong sulphuric acid.	Dull violet colour, changing to fine red-violet on adding a trace of sodium nitrite.	Red-brown.
Colour of solution in alkali hydroxide.	Violet (but redder than an alkalinesolution of alizarin); 2 absorption-bands simulating those of alizarin.	Purple (redder shade than with anthrapurpurin); on dilution, pure red. 2 absorption-bands, more refrangible than those of alizarin, and a characteristic broad band in in the blue.
Colour of solution in ammonia.	Violet; no absorption-bands.	Yellowish-red; no absorption-bands.
Colour of solution in sodium carbonate.	Violet.	Yellowish-red.
Reaction with alcoholic solution of lead acetate.	Purple precipitate, dissolving with violet colour on boiling with excess of the reagent.	Reddish-brown precipitate, dissolving very sparingly on boiling with excess of the reagent, with red colour.
Reaction with alcoholic solution of cupric acetate.	Fine violet colour.	Red colouration.

Anthrapurpurin and Flavopurpurin are now met with in commerce in a state of purity. For the detection of impurities in commercial Flavopurpurin, Jellinek recommends that the sample should be dissolved in alkali and the solution treated with lead acetate. The precipitate is well washed with hot water and decomposed by sulphuric acid in presence of alcohol. The colouring matter is then obtained from the alcoholic solution by fractional crystallisation. *Alizarin* 3 *S* is a sodium monosulphonate of Flavopurpurin.

The following table exhibits the characteristic differences between alizarin and the three purpurins:

Substance	With NaOH	With H_2SO_4	Sublimation point
Alizarin.........	Blue-violet.......	Brown-red.......	Below 160°.
Anthrapurpurin..	Violet...........	Brown...........	At 160°
Flavopurpurin...	Purplish-red......	Red-violet........	At 170°.
Purpurin	Red.............	Cherry-red.......	At 150°.

Fibres dyed with alizarin or flavopurpurin lakes or with the aluminium lake of anthrapurpurin are not changed in an alkaline solution of potassium ferricyanide, whereas the colour on fibres dyed with anthrapurpurin on an iron mordant, or with purpurin are destroyed.

Commercial Alizarin. Alizarin Paste. V and G.

Commercial alizarin always occurs in the form of an ochre-yellow or brownish-yellow paste,[1] consisting of the solid colouring matters in a hydrated state mixed with a definite proportion of water.

Alizarin paste ordinarily contains 20% or 40% of solid matter. The strength is easily ascertained by drying a fair sample at 100°. By exposure to this temperature the alizarin is rendered anhydrous, loses the slight solubility it previously possessed, and becomes wholly unfit for dyeing.[2] The *residue*, after drying, should be yellow—not dark brown. After weighing, the residue should be ignited at a dull red heat. The *ash* obtained should not exceed 1% of the weight of the dried residue, and should be practically free from *iron*.[3]

According to Benedikt and Knecht, "*Chemistry of Coal Tar Colours*" London, 1886, commercial alizarin is liable to contain glycerin, turkey-red oil, and other thickening agents, for the detection of which they recommended dilution of the paste with water and filtration of the liquid, when a perfectly colourless filtrate should be obtained, which may contain small quantities of sodium chloride and other salts, but should leave no syrupy residue of glycerin on cautious evaporation. A practical objection to this method of examination exists in the great difficulty, sometimes amounting to impossibility, which attends the filtration of alizarin paste diluted with water. If the presence of glycerin or turkey-red oil be suspected, it would probably be preferable to examine the residue left on evaporating the paste to dryness at 100°.

[1] Dry alizarin may be prepared by mixing the paste with starch and pressing and drying.

[2] The same statement applies to alizarin paste which has been frozen, and hence it is customary during severe weather to protect the colouring matter from the cold.

[3] The so-called "soluble alizarin" consists of sodium boro-alizarate. It is prepared by dissolving 1 part of alizarin and 2 parts of borax in boiling water, and evaporating the solution to dryness. It is said that a solution of soluble alizarin in distilled water gives a very delicate test for the presence of lime in water, a flocculent precipitate being formed with the merest trace of calcium salt.

Besides true alizarin, the commercial paste contains more or less of the dihydroxyanthraquinones isomeric with alizarin, as well as several of the mono- and trihydroxyanthraquinones. All these substances present a very close general resemblance to alizarin proper, but all except the trihydroxyanthraquinones (flavopurpurin and anthrapurpurin) are valueless as dyes, and these latter give very different shades from those produced by pure alizarin.

The following method is given by Benedikt and Knecht for recognising the constituents of commercial alizarin paste: A small quantity of the sample is dissolved in a solution of sodium carbonate, and the liquid filtered. The residue consists of *anthraquinone* and *monohydroxyanthraquinone*, which may be separated by means of dilute sodium hydroxide solution, in which only the latter is soluble. The filtered carbonate of sodium solution is acidified with hydrochloric acid, and the precipitate boiled with milk of lime, which will dissolve any *anthraflavic* and *isoanthraflavic acids* with red colour.[1] On filtering and acidifying the filtrate these impurities will be reprecipitated, and may be collected, washed, and weighed. The insoluble lime-lake is removed from the filter and decomposed by agitation with dilute hydrochloric acid, and the separated colouring matter washed and weighed, or dissolved in ether and recovered by evaporating the ethereal solution. The residue thus obtained will contain the alizarin of the sample, mixed with any anthrapurpurin or flavopurpurin which may be present.

[1] Both these bodies, as also monohydroxyanthraquinone, are valueless as dyes. Their presence in commercial alizarin may be detected by boiling the sample with milk of lime and filtering, when a yellow or brownish-red solution will be obtained. The following are the chief differences between these three allied substances:

	β-Monohydroxy-anthraquinone	Anthraflavic acid	Isoanthraflavic acid
Action of heat.	Sublimes, without melting, above 285°.	M. p. above 330°, and sublimes.	M. p. above 300°, and sublimes.
Action of water.	Easily soluble; insoluble in acidified water.	Insoluble.	Insoluble.
Action of aqueous alcohol.	Separates from hot solution in yellow laminæ or needles.	Separates from solution in long, anhydrous yellow needles or laminæ.	Separates from solution in hydrated crystals.
Action of hot, strong, sulphuric acid.	....	Forms yellow solution.	Forms deep red solution.
Action of cold baryta water.	Soluble with reddish-yellow colour.	Insoluble.	Easily soluble with dark red colour.
Action of hot lime water.	Soluble with reddish-yellow colour.	Slightly soluble, cold; nearly insoluble, hot; solution yellowish-red.	Easily soluble with dark red colour.

According to Schunck and Römer, the detection and approximate estimation of these 3 substances bodies in admixture can readily be effected as follows: The mixture is dried at 100°, and then placed between 2 glass plates, separated from each other by a leaden ring some millimetres in thickness. The whole is heated in an air-bath to 130°–150°,

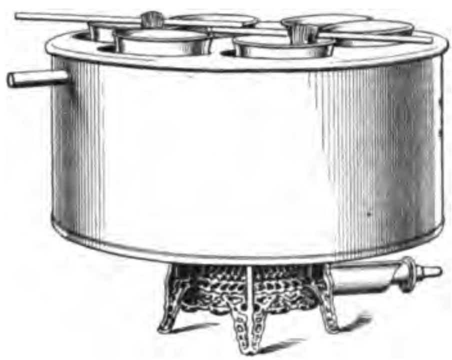


FIG. 5.

at which temperature the *alizarin* alone sublimes. On raising the temperature to 170°, a crystalline sublimate of mixed *flavopurpurin* and *anthrapurpurin* is obtained, the former of which assumes the shape of fine reddish-yellow needles, while the latter sublimes in compact, well-defined rhombic crystals. A separation of the 2 isomers may be effected by boiling with benzene, in which only flavopurpurin dissolves.[1]

[1] For the analysis of alizarin pastes as obtained from filter presses, the percentage of *moisture* is determined by evaporating a weighed sample in a flat platinum dish at 100°. After weighing, the *inorganic matter* present is determined by incineration. Usually the ash, which should not exceed 0.2% in a 20% paste, consists of either sodium or calcium salts but sometimes lead and iron are also present, though contamination of alizarin with iron should be carefully avoided if in dyeing bright shades are required. The *tinctorial properties* of the paste are then compared with those yielded by a standard sample of known strength and shade. In this operation a special 5-striped cotton cloth is best employed the mordants on which consist of strong and weak aluminium and iron salts and a mixture of the two respectively. Of this, 10-in. lengths are most suitable. The dye vessels, preferably of glass or porcelain, and of about 600 c.c. capacity, are arranged in rows in a suitable copper water-bath heated with gas (see figure 5). 5 grm. of the 20% paste under examination is suspended in a litre of water and 50–70 c.c. of this, together with 4 c.c. of a 1% solution of calcium acetate are added to 500 c.c. of water in the dye vessel. The temperature is gradually raised to 80° during 1 hour, the heat being maintained at that temperature for half an hour. After washing in cold water, the fents are well beaten with a wooden mallet and again rinsed, the treatment being continued until the loosely adhering particles of alizarin are almost entirely removed. This is followed by two soaping operations, each lasting 1 hour, the first at 60° and the second at 80°, conducted in a large tinned copper vessel, which contains for each fent a solution of 0.5 grm. of curd soap in a litre of water. The patterns after washing are dried at the ordinary temperature. Swatches of turkey-red cloth are very frequently dyed, and these, after the ordinary soaping, are heated under pressure with soap solution, to which a trace of stannous chloride has been added to give them a more brilliant appearance.

m-Hydroxyanthraquinone may be detected by treating a hot alkaline solution with baryta water and filtering the precipitate. A red coloured filtrate is obtained which on acidification deposits a yellow precipitate.

Anthra- and isoanthraflavic acids. To a sample of the paste suspended in boiling water barium hydrate is added and the barium lake filtered off. A red coloured filtrate giving a yellow precipitate on neutralisation indicates the presence of these substances.—Perkin (*J. Soc. Dyers, etc.*, 1897, 13, 81).

Commercial name	Formula	Remarks
Alizarin Yellow C.	$C_6H_2\begin{cases}(1)OH\\(2)OH\\(3)OH\\(4)CO.CH_3\end{cases}$	From pyrogallol.
Alizarin Yellow A.	$C_6H_5(1)CO(1)C_6H_2\begin{cases}(2)OH\\(3)OH\\(4)OH\end{cases}$	From pyrogallol.
Alizarin V, VI, P, No. 1, Ie. Alizarin for violet.	$C_6H_4\left\{\begin{matrix}(2)CO(2)\\(3)CO(3)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1)OH\\(6)OH\end{matrix}\right.$	From anthraquinone-monosulphonic acid.
Alizarin RG, GI, SDG, X, No. 10, CA. Flavopurpurin.	$C_6H_3\left\{\begin{matrix}(2)CO(2)\\(5)OH\\(3)CO(3)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1)OH\\(6)OH\end{matrix}\right.$	From α-anthraquinone-disulphonic acid.
Alizarin SC, SX, GD, RX, SC, SX extra, RF. Anthrapurpurin.	$C_6H_3\left\{\begin{matrix}(2)CO(2)\\(6)OH\\(3)CO(3)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1)OH\\(6)OH\end{matrix}\right.$	From β-anthraquinone-disulphonic acid.
Alizarin No. 6. Purpurin.	$C_6H_4\left\{\begin{matrix}(2)CO(2)\\(3)CO(3)\end{matrix}\right\}C_6H\left\{\begin{matrix}(1)OH\\(4)OH\\(6)OH\end{matrix}\right.$	From alizarin by oxidation.
Alizarin Orange A, OR, OG, N, AO, AOP.	$C_6H_4\left\{\begin{matrix}(2)CO(2)\\(3)CO(3)\end{matrix}\right\}C_6H\left\{\begin{matrix}(1)OH\\(5)NO_2\\(6)OH\end{matrix}\right.$	From nitrated alizarin.
Anthracene Brown. R, G. Alizarin Brown. Anthragallol.	$C_6H_4\left\{\begin{matrix}(2)CO(2)\\(3)CO(3)\end{matrix}\right\}C_6H\left\{\begin{matrix}(1)OH\\(5)OH\\(6)OH\end{matrix}\right.$	From gallic acid.
Galloflavin.	$C_{13}H_6O_9$ (constitution not known).	From gallic acid.
Alizarin Black S, SW. Alizarin Blue-Black SW. Naphthazarin S.	$C_{10}H_4\begin{cases}(1)O\\ \quad\vert\\(4)O \quad + NaHSO_3\\(7)OH\\(8)OH\end{cases}$	From dinitronaphthalene.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Yellow paste; yellow solution.	Brown.	....	Yellow.	....	Soluble in alcohol.
Yellow paste; yellow solution.	Deeper yellow.	No change.	Yellow.	White ppt.	....
Yellow paste; insoluble in cold water; slightly soluble in hot water.	Violet.	No change.	Orange.	Orange ppt.	On cotton mordanted: Al—red. Fe—violet. Cr—brown.
Yellow paste; slightly soluble in boiling water.	Violet.	....	Brown.	Orange ppt.	Al—red. Soluble in alcohol. With ammonia brown solution.
Yellow paste; slightly soluble in boiling water.	Violet.	....	Red.	Orange ppt.	Al—red. With ammonia violet solution.
Brown paste; slightly soluble in hot water.	Magenta-red.	....	Orange.	Brown ppt.	Soluble in alcohol. Al—red. Fe—purple. Cr—brown.
Brown paste; insoluble in hot or cold water.	Magenta-red solution.	....	Yellow.	Yellow ppt.	Soluble in acetic acid. Al—orange. Fe—red-violet. Cr—red-brown.
Brown paste; insoluble in water.	Greenish-blue solution.	No change.	Brown.	Brown ppt.	Solution in alcohol. Cr—brown.
Yellow paste; insoluble in water.	Yellowish-brown solution.	No change.	Orange.	Grey ppt.	Cr—greenish-yellow. Slightly soluble in boiling alcohol.
Black paste; soluble in hot water.	Blue.	Brownish-red.	Yellow; on heating red, SO_2 evolved.	Black ppt.	Soluble in alcohol. Cr—black.

Commercial name	Formula	Remarks
Alizarin Blue. Alizarin Blue R, G-W, A, DN-W, F, R, RR, AB.	$C_6H_4\left\{\begin{array}{l}(2)CO(2)\\(3)CO(3)\end{array}\right\}C_6\left\{\begin{array}{l}(1)OH\\(6)OH\\(4)CH=CH\\(5)N=CH\end{array}\right.$	From β-nitro-alizarin.
Alizarin Yellow.	$C_{14}H_{10}O_{10}$	From ellagic acid.
Anthracene Yellow.	$C_6\left\{\begin{array}{l}(1)OH\\(2)O——CO\\(3)C(CH_3)=CH\\(4)Br\\(5)Br\\(6)OH\end{array}\right.$	From pyrogallol.
Alizarin Bordeaux B, BD, G, GG.	$C_6H_2\left\{\begin{array}{l}(1)OH\\(2)CO(2)\\(3)CO(3)\\(4)OH\end{array}\right\}C_6H_2\left\{\begin{array}{l}(1)OH\\(6)OH\end{array}\right.$	Oxidation of alizarin.
Alizarin Cyanin R.	$C_6H_2\left\{\begin{array}{l}(1)OH\\(2)CO(2)\\(3)CO(3)\\(4)OH\end{array}\right\}C_6H\left\{\begin{array}{l}(1)OH\\(4)OH\\(6)OH\end{array}\right.$	Oxidation of Alizarin Bordeaux.
Alizarin Cyanin G.		Treatment of preceding with air and ammonia.
Alizarin Red S. Alizarin Carmine. Alizarin WS, W, SA.	$C_6H_4\left\{\begin{array}{l}(2)CO(2)\\(3)CO(3)\end{array}\right\}C_6H\left\{\begin{array}{l}(6)OH\\(5)OH\\SO_3Na\end{array}\right.$	From alizarin with concentrated H_2SO_4.
Alizarin Maroon.	$C_6H_4\left\{\begin{array}{l}(2)CO(2)\\(3)CO(3)\end{array}\right\}C_6\left\{\begin{array}{l}(1)OH\\(4)OH\\(5)NH_2\\(6)OH\end{array}\right.$	From nitroalizarin.
Alizarin Blue S. Alizarin Blue Soluble Powder ABS. Anthracene Blue S.	$C_6H_4\left\{\begin{array}{l}(2)C\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right\}(2)\\(3)C\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right\}(3)\end{array}\right\}C_6(OH)_2\left\langle\begin{array}{l}N=CH\\CH=CH\end{array}\right.$	From Alizarin Blue.
Alizarin Indigo Blue S.	$\left.\begin{array}{l}HO(1)\\HO(4)\\HO(6)\end{array}\right\}C_6H\left\{\begin{array}{l}(2)C\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right\}(2)\\(3)C\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right\}(3)\end{array}\right\}C_6(OH)_2\left\langle\begin{array}{l}N=CH\\CH=CH\end{array}\right.$	From Alizarin Green.
Alizarin Green S.	$\left.\begin{array}{l}HO(1)\\HO(4)\end{array}\right\}C_6H_2\left\{\begin{array}{l}(2)C\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right\}(2)\\(3)C\left\{\begin{array}{l}OH\\SO_3Na\end{array}\right\}(3)\end{array}\right\}C_6(OH)_2\left\langle\begin{array}{l}N=CH\\CH=CH\end{array}\right.$	From Alizarin Blue.

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Blue crystals; insoluble in water.	Green in alcohol solution.	Orange in alcohol solution.	Carmine-red.	Orange.	Al—bluish-violet Fe—greenish-blue. Cr—India-blue. Soluble in alcohol
Brown paste; insoluble in water.	Brown solution.	....	Brown.	Ellagic acid ppt.	Slightly soluble in alcohol.
White paste; slightly soluble in water.	Brown solution repptd. by acids.	....	Brown.	....	....
Red paste; insoluble.	Violet solution.	....	Violet.	Red ppt.	Al—bordeaux. Cr—violet-blue.
Brown paste; insoluble.	Blue solution.	....	Blue solution.	....	Al-violet. Cr—blue.
Black paste: insoluble.	Greenish-blue solution.	....	Red.	....	Soluble in alcohol. Al—blue. Cr—bluish-green.
Orange powder; orange solution.	Violet.	Yellow.	Orange.	Yellow.	Soluble in alcohol. Al—scarlet. Cr—bordeaux.
Violet paste; insoluble.	Violet solution.	No change.	Red.	....	Al—garnet.
Brown powder; brown solution.	Violet.	Orange.	Yellow.	Brown ppt.	Cr—blue.
Dark brown paste; red solution.	Blue.	Blue ppt. on boiling.	....	....	Cr—indigo-blue.
Dark brown paste; soluble in cold water.	Violet.	....	....	....	Cr—bluish-green.

Commercial name	Formula	Remarks
Rufigallol.	$\left.\begin{matrix} HO(1) \\ HO(4) \\ HO(5) \end{matrix}\right\} C_6H \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6H \left\{\begin{matrix} (1)OH \\ (5)OH \\ (6)OH \end{matrix}\right.$	From gallic acid.
Fast Black B.	Not determined.	From dinitronaphthalene.
Fast Black BS.	Not determined.	From Fast Black B.
Alizarin Garnet R. Alizarin Cardinal.	$C_6H^4 \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6H \left\{\begin{matrix} (1)OH \\ (6)OH \\ (4)NH_2 \end{matrix}\right.$	From benzoylalizarin.
Alizarin Orange G.	$HO(5)C_6H_3 \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6H \left\{\begin{matrix} (1)OH \\ (6)OH \\ (5)NH_2 \end{matrix}\right.$	From flavopurpurin.
Alizarin Black P.	$HO(5)C_6H_3 \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6(OH)_2 \left\langle\begin{matrix} N - CH \\ \quad\quad\vert \\ CH = CH \end{matrix}\right.$	From aminoflavopurpurin.
Alizarin Black S.	Not determined.	From Alizarin Black P.
Anthracene Blue WR.	$\left.\begin{matrix} HO(1) \\ HO(4) \\ HO(6) \end{matrix}\right\} C_6H \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6H \left\{\begin{matrix} (1)OH \\ (4)OH \\ (5)OH \end{matrix}\right.$	From dinitroanthraquinone.
Anthracene Blue WG.	Not determined.	From dinitroanthraquinone.
Anthracene Blue WB.	Not determined.	From dinitroanthraquinone.
Acid Alizarin Blue BB, GR.	$\left.\begin{matrix} SO_3Na(6) \\ HO(1) \\ HO(4) \\ HO(5) \end{matrix}\right\} C_6 \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6 \left\{\begin{matrix} (1)OH \\ (4)OH \\ (6)OH \\ (5)SO_3Na \end{matrix}\right.$	....
Acid Alizarin green B, G.	$\left.\begin{matrix} SH(1) \\ HO(4) \\ HO(6) \\ SO_3Na(5) \end{matrix}\right\} C_6 \left\{\begin{matrix} (2)CO(2) \\ (3)CO(3) \end{matrix}\right\} C_6 \left\{\begin{matrix} (4)SH \\ (1)OH \\ (5)OH \\ (6)SO_3Na \end{matrix}\right.$	....
Alizarin Dark Green.		Naphthazarin melt and phenols.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Red powder; insoluble in water.	Blue solution.	No change.	Red.	....	Cr—brown.
Dark blue paste; insoluble in water.	Violet solution in hot NaOH.	....	Green.	....	Direct dye for cotton.
Black paste; violet solution.	....	....	Green.	....	Soluble in alcohol. Dyes cotton in cold bath.
Red paste; insoluble in water.	Red solution	Brown.	Brown.	Red ppt.	Soluble in alcohol. Al—bluish-red.
Orange paste; insoluble in water.	Violet.	Brighter.	Orange.	Orange ppt.	Soluble in alcohol. Al—orange.
Black paste; insoluble in water.	Green.	Brown.	Brown.	Brown ppt.	Soluble in alcohol. Cr—violet-grey.
Dark brown paste; brown solution.	Violet.	Black ppt.	Brown.	Brown ppt.	Cr—grey.
Brown paste; insoluble.	Blue.	....	Violet.	....	Soluble in alcohol. Al—violet.
Dark blue paste; violet solution in hot water.	Green.	....	Brown.	....	Al—blue.
Dark Blue paste: insoluble in water	....	....	....	....	Al—greenish-blue.
Red crystals; red solution.	Violet.	No change.	Violet.	Red.	Acid dye for wool.
Dark red crystals; green solution.	Violet.	Violet.	Blue.	Violet.	Acid dye for wool.
Greyish-brown powder; violet solution.	Greenish blue.	....	Violet.	Redder; dark ppt.	On chrome mordanted wool.

The foregoing table shows the characters of different varieties of alizarin and analogous colouring matters met with in commerce in the form of paste.

In forming an opinion on the quality of commercial alizarin, a dye-test is comparative useful, and is best conducted as follows: A length of white calico, 4 in. wide, is boiled in water containing a little sodium hydroxide, to remove any stiffening agents. After being thoroughly washed, it is immersed in a solution of aluminium acetate ("red-liquor") of known volume and concentration, the time of immersion and the temperature being duly noted. The calico is then removed, wrung out, and torn into a number of strips 3 in. wide, which are hung to drain. 0.5 grm. of each sample of alizarin paste to be tested is then weighed out and put into a corresponding number of wide-mouthed beakers or dye pots of similar size arranged in a suitable water-bath.[1] 1,000 c.c. of water at 40° is then poured into each, and the liquid well agitated to facilitate the solution of the alizarin. A strip of the previously mordanted calico of known or calculated weight is then immersed in the contents of each vessel, care being taken that it is suspended freely so that all parts are kept in contact with the liquid. This is best done by attaching it to a thread tied to a glass rod placed across the mouth of the beaker or dye pot. The temperature of the bath is then gradually raised, so that it may reach 75° in about an hour and a half from the immersion of the cloth, after which the temperature is increased to about 90° for half an hour longer. The strips of calico are now withdrawn, rinsed in cold water, and dried. Each strip should then be cut into equal portions, one of which is preserved, while others are steeped for half an hour at about 40°–42° in 1 litre of water containing 2 grm. of white curd soap.[2] The strips are then taken out, rinsed in cold water, and put into another bath made with the same quantities of soap and water, with the addition of 0.6 grm. of stannous chloride ("tin crystals"), which is allowed to boil for 30 minutes. The strips are then removed, well rinsed, dried, and preserved for reference.

Instead of relying on the behaviour of the dyestuff with a single mordant, it is preferable to use a piece of cloth printed in 5 or 6

[1] A very convenient apparatus for the dyeing of small samples consists in an enamelled vessel which may be heated directly over a small Fletcher burner. Either a litre or a half-litre vessel may be employed. Two stirring rods of glass may be used for the purpose of working the material (either yarn or cloth) in the bath.

[2] In some cases, as in the assay of reds, it is desirable to precede the soap treatment by an oil process. This consists in immersing the fabric in a 5% solution of turkey-red oil, again drying the cloth, and then exposing it to open steam in a suitable box for 1 hour.

parallel lines with, *e. g.*, (*a*) strong solution of aluminium acetate; (*b*) weak aluminium acetate; (*c*) strong iron acetate; (*d*) weak iron acetate; (*e*) mixture of strong solutions of aluminium and iron acetates; (*f*) mixture of weak solutions of aluminium and iron acetates.[1]

The shades dyed by commercial alizarin depend much on the composition of the colouring matter. Thus the variety giving blue shades (*e. g.*, "*Alizarin V*, or extreme blue shade") consists chiefly of real alizarin. In dyeing, it yields with alumina mordant a bluish but not very brilliant shade of red; but with a small proportion of mordant very beautiful shades of pink can be obtained. When mordanted with iron, it is used for dyeing and printing fast violets. The yellow shades of commercial alizarin (*e. g.*, Alizarin G) contain a large percentage of Anthrapurpurin and Flavopurpurin, and but little alizarin. Anthrapurpurin yields an almost neutral red with alumina mordants; but Flavopurpurin gives a fiery red containing a considerable proportion of yellow, and hence the larger the proportion of flavopurpurin the yellower the shade. Iron mordants give with anthrapurpurin and flavopurpurin violets of little or no practical value. Purpurin does not occur in artificial alizarin, but was a very common constituent of the dye from madder, which was the chief reason of the different shades produced by natural and artificial alizarin.

Detection of Alizarin and its Allies on the Fibre.

Alizarin and other allied colouring matters are applied in so many ways, and with such a variety of mordants, that it is not possible to describe the method of dyeing shortly. As the use of a mordant is essential, they are not so suitable for silk as the substantive coal-tar dyes. Alizarin is used in wool-dyeing, not merely as a bottoming colour for indigo, etc., but as a self-colour with mordants. Thus when mordanted with alum and tartar it gives fine reds and scarlets; with stannous chloride, orange shades; with potassium dichromate, rich claret-browns; with ferrous sulphate, shades ranging from bluish-violet to black; with nickel ammonium sulphate, grey; and with uranium acetate, slate-blue shades. These colours are fast to light and air, and resist milling.

The mordants used in dyeing cotton with alizarin are various

[1] Pieces of cloth printed in the manner recommended, or any other which may be desired, can be obtained by order from many calico-printers.

compounds of calcium, aluminium, iron, chromium and tin, besides tannic acids and oils. *Turkey-red*, one of the fastest and most perfect of the alizarin styles, is dyed by a complicated series of operations, in which the formation of a compound of alumina with alizarin and a fatty acid is an essential step. Treatment with ether changes cloth dyed turkey-red to a dull cherry-red colour, and on evaporating the ethereal solution a brilliant scarlet semi-solid residue is left. This dissolves in hot sodium hydroxide solution with purplish-blue colour, and on adding hydrochloric acid alizarin is precipitated in orange flakes. *Alizarin Violet* may be obtained in a similar manner to turkey-red, the blue shade of alizarin being used for its production. Other violets are obtained by the use of an iron mordan (see page 119).

Turkey-red is but little affected by a dilute solution of bleaching powder if free acid be absent, but the other alizarin colours are gradually bleached.

Alizarin is not affected by potassium dichromate, but free chromic acid destroys it. Dilute solutions of permanganate (1%) and alkaline solutions of ferricyanides are without effect on colours produced by artificial alizarin, but *purpurin* is easily oxidised. The last reagent especially is of value for distinguishing colours produced by artificial alizarin from those produced by madder, as the latter always contains purpurin. Madder-dyed fibres are also distinguished by boiling them with a strong solution of alum, when the purpurin is dissolved with formation of a reddish-yellow liquid, which exhibits a strong greenish-yellow fluorescence and characteristic absorption-bands (page 135).

On exposure to nitrous fumes, cloth dyed with Alizarin-Red becomes orange, from formation of nitro-alizarin.

Fibres dyed with alizarin are but little affected when boiled with ammonia or sodium hydroxide solution of moderate strength. Alizarin Red is turned violet when boiled with baryta water. Dilute acids are almost without action. Concentrated hydrochloric acid decomposes the colour lakes, and partially or completely removes the metallic oxides. The violets are more readily affected than the reds, and of the latter turkey-red offers the greatest resistance.

Cold concentrated sulphuric acid dissolves the fibre of cotton as well as the colouring matter. On diluting the solution with water, the alizarin, etc., will be thrown down as a flocculent precipitate, which may be dissolved by agitation with ether. The separated ethereal solution on evaporation will leave a residue, in which alizarin and its

associates may be recognised by their appearance on sublimation, the colour and absorption-spectra of their alkaline solutions, etc.

Fabrics dyed with alizarin are decolourised when boiled with a mixture of 2 parts of alcohol and 1 of strong hydrochloric acid. This behaviour distinguishes *Alizarin Black* from *Aniline Black*, which latter colour is unaffected, or merely turned greenish, by similar treatment. *Logwood blacks*, on the other hand, are destroyed even by dilute acids, which acquire a red colour.

Strong acid oxidising agents, such as nitric acid and ferric chloride, destroy alizarin colours.

Chrysophanic Acid, Etc.

Chrysophanic Acid. $C_{15}H_{10}O_4$. This substance occurs in rhubarb root, of which it is one of the main constituents, but it appears not to be the active principle of this drug. According to Tutin and Clewer (Trans. 1910, **97**, 6,) it is probably 1-methyl-chrysazin

$$OH.C_6H_3\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle C_6H_2(CH_3).OH.$$

It can be extracted from rhubarb root by means of ether; as so obtained it is always accompanied by methylchrysophanic acid, which causes the m. p. of the product to be sometimes as low as 154°. (Compare Oesterle and Johann, *Arch. Pharm.*, 1910, **248**, 476-500.) The pure acid melts at 186–188° (Hesse, *Annalen*, 1899, **309**, 36). It crystallises in small yellow scales. It is not immediately soluble in ammonia, but gradually chemical action takes place with production of a purple solution. Solutions of similar colour are obtained at once with aqueous alkali hydroxides. It is insoluble in alkali carbonate solution. E. P. Alvarez (*Ann. Chim. Anal.*, 1907, **12**, 9) gives the following reaction: 0.05 to 0.1 grm. of the substance are placed in a porcelain dish with 0.2 to 0.3 grm. of sodium peroxide and 5 c.c. of alcohol. After 4 to 6 minutes 15 c.c. of water are added. Chrysophanic acid gives a cherry-red colouration, becoming brighter on adding the water. Under the same conditions chrysarobin (*vide infra*) gives the colour of lees of wine, which persists on adding the water and is changed by acetic acid to yellow.

Chrysarobin, $C_{15}H_{12}O_3$, is obtained from *Araroba* or *Goa* powder by extraction with certain solvents such as chloroform or

ether. These substances are the secretions of certain trees. A large amount of chrysarobin is sold as "chrysophanic acid," but contains none of that substance, which can, however, be obtained from it by oxidation in alkaline solution (Oesterle, *Arch. Phar.*, 1905, **243**, 434). Chrysarobin is the anthranol corresponding to chrysophanic acid, and has the formula

$$OH.C_6H_2(CH_3)\left\langle\begin{matrix} C(OH) \\ C(OH) \end{matrix}\right\rangle C_6H_3.OH.$$

The crude product is used in the treatment of skin diseases. Pure chrysarobin consists of lemon-yellow scales, m. p. 202°. It is insoluble in sodium carbonate solution. Its alkaline solution becomes brown on adding ferric chloride.

The following are the chief differences between chrysarobin and chrysophanic acid:

	Chrysarobin	Chrysophanic acid
Action of ammonia.........	Insoluble..................	Slowly soluble with red colour.
Action of very dilute potassium hydroxide solution.	Undissolved at first. On agitation with air, dissolves with red colour.	Soluble with red colour.
Action of strong potassium hydroxide solution.	Soluble with yellow colour and strong green fluorescence. On exposure to air, colour changes rapidly to red.	Soluble with red colour.
Action of fusing potassium hydroxide.	Brown colouration..........	Blue colouration.
Action of concentrated sulphuric acid.	Soluble with yellow colour ..	Soluble with red colour.

According to J. Agema, commercial chrysophanic acid may be purified by dissolving it in chloroform and adding an equal volume of rectified spirit, when the pure acid only is precipitated.

Exposure to a temperature of 195° converts chrysophanic acid into a substance allied to purpurin, which colours alum mordants pomegranate-red and iron mordants a light greenish-blue. It is nearly insoluble in water, but dissolves sparingly in hot alcohol (1 in 224), the greater part separating on cooling. Chrysophanic acid is also readily soluble in ether, chloroform, benzene, petroleum spirit,

amyl alcohol, and glacial acetic acid, the solutions being yellow or brownish-yellow.

Chrysophanic acid is precipitated in yellow flakes on neutralising its alkaline solutions. A very small quantity of alkali suffices for the production of the red colour. If the red solution of chrysophanic acid in alkali hydroxide be evaporated to dryness, it turns violet and blue during the operation. The films deposited on the sides of the vessel especially exhibit this change of colour.

If a solution of chrysophanic acid in ether, chloroform, benzene, amyl alcohol, or petroleum spirit be shaken with solution of sodium hydroxide, the colouring matter passes completely or partially into the aqueous liquid, which it colours pink or crimson. Ammonia gives the same reaction as sodium hydroxide with a solution of chrysophanic acid in ether or petroleum spirit, but does not readily extract the colouring matter from its solution in chloroform or benzene.

The acid characters of chrysophanic acid are but feebly marked. It forms unstable barium and lead salts, which are decomposed even by carbonic acid. An ammoniacal solution of chrysophanic acid forms a lilac precipitate with acetate of lead, and a rose-coloured precipitate with alum.

Chrysophanic acid is not acted on by dilute nitric acid, but the strong acid converts it into tetranitro-chrysophanic acid, $C_{15}H_6(NO_2)_4O_4$, a compound homologous with chrysamic acid, obtained by the action of nitric acid on aloes or chrysazin.

When heated with acetic anhydride and sodium acetate chrysophanic acid yields a diacetyl-derivative.

When heated with zinc-dust, chrysophanic acid is reduced to methyl-anthracene, $C_{15}H_{10}$, just as alizarin and chrysazin yield anthracene, $C_{14}H_8$, when similarly treated.

Chrysophanic acid possesses decided antiseptic properties, and has proved of service in the treatment of certain forms of skin disease. It is said to be somewhat uncertain in its action, a fact which is possibly due to an admixture of chrysarobin, to the deoxidising action of which impurity it has been suggested that the chrysophanic acid of commerce owes its chief value.

Chrysophanic acid is said to produce purplish-brown stains on linen or cotton, which are only removable with difficulty, prolonged immersion of the fabric in a solution of bleaching-powder being the best mode of treatment. It is doubtful whether these stains are pro-

duced except in the presence of an alkali. A solution of chrysophanic acid in alcohol, acetic acid, or petroleum spirit merely colours linen a light yellow colour. On washing the stained fabric with soap, the purplish-brown stain is readily developed.[1]

An aqueous or alcoholic solution of chrysophanic acid does not dye silk or wool yellow.

Chrysophanic acid is said to be liable to adulteration with picric acid and other yellow colouring matters. Inorganic adulterants may be detected by igniting a portion of the sample. *Picric acid*, if present, would be detected by the yellow colouration the sample imparts to cold water; by the yellow crystalline precipitate produced on adding potassium carbonate to the alcoholic solution of the sample; and by immersing a piece of white wool in the hot aqueous solution, which, in presence of picric acid, will be dyed yellow. *Aurin* or *rosolic acid* might be detected in chrysophanic acid by treating the sample with chloroform or benzene, which would dissolve the chrysophanic acid without affecting the adulterant.

Good rhubarb yields a colourless extract even when left for several days in contact with petroleum spirit, while a rhapontic rhubarb yields an intensely yellow extract. According to Rochleder (*Chem. News*, **20**, 78), the acid from rhubarb generally contains emodin, $C_{15}H_{10}O_5$. This substance has the constitution of a tri-hydroxymethyl-anthraquinone, and hence is homologous with purpurin. It occurs to a notable extent in the bark of *Rhamnus frangula*, and may be separated from chrysophanic acid by means of sodium carbonate, which dissolves the emodin only, with blood-red colouration. It forms long, brittle, monoclinic prisms, m. p. 245°–250°, and is converted into methylanthracene by heating with zinc-dust.

A substance having considerable analogy to chrysophanic acid occurs in the root of the Mexican plant *Trixis pipitzahuac* or *Perezia fructicosa*. This substance which has been named pipitzahoic acid, has the formula $C_{15}H_{20}O_3$, and dissolves in alkalies with a colour resembling that of potassium permanganate (Anschütz and Leather, *J. Chem. Soc.*, 1886, **49**, 709).

[1] Evidently, the production of chrysophanic acid stains on linen may be avoided by dissolving out the colouring matter and grease with benzene.

DYESTUFFS OF GROUPS 6 TO 12.

Group 6. Diphenylmethane and Triphenylmethane Dyes.
Group 7. Pyrone, Xanthone and Fluoran Dyes.
Group 8. Indamines and Indophenole Dyes.
Group 9. Azine Dyes.
Group 10. Oxazine and Thiazine Dyes.
Group 11. Quinoline and Acridine Dyes.
Group 12. Thiazole and Sulphur Dyes.

6. DIPHENYLMETHANE AND TRIPHENYLMETHANE COLOURING MATTERS.

BY J. T. HEWITT, M. A., Ph. D., D. Sc., F. R. S.

Diphenylmethane, $CH_2(C_6H_5)_2$, and triphenylmethane, $CH(C_6H_5)_3$, form the starting-point of a large number of organic dyestuffs. The numerous derivatives of the aurins, phthaleins and rosanilines may be classified under these two parent substances.

Both hydrocarbons are colourless although they exhibit selective absorption in the ultra-violet, and introduction of amino- or hydroxyl-groups does not shift the absorption into the visible part of the spectrum, though if these substituted derivatives are oxidised, colouring matters of quinonoid structure are obtained. This is easily seen by a comparison of triphenylmethane, paraleucaniline and pararosaniline (as hydrochloride).

$$C\begin{cases}.C_6H_5\\.C_6H_5\\.C_6H_5\\.H\end{cases}\qquad C\begin{cases}.C_6H_4.NH_2\\.C_6H_4.NH_2\\.C_6H_4.NH_2\\.H\end{cases}\qquad C\begin{cases}.C_6H_4.NH_2\\.C_6H_4.NH_2\\:C_6H_4:NH_2Cl\end{cases}$$

Colourless. Colourless. Red.

Diphenylmethane is the parent substance of a few dyestuffs. In the auramines the methane residue has become a ketone-imide group, while each of the benzene nuclei is substituted in the para position by alkylated amino-groups. Auramine is obtained from tetramethyl-

diaminobenzophenone (Michler's ketone), the product of the interaction of carbonyl chloride and dimethylaniline, by replacing the oxygen atom by the :NH residue. This is effected by heating to 150°–170° with ammonium chloride and zinc chloride. If in place of ammonium chloride the hydrochlorides of aniline and allied bases are employed, substituted auramines are produced. The relationship of the substances mentioned are seen from the following formulæ:

Diphenylmethane	$CH_2(C_6H_5)_2$
Benzophenone	$CO(C_6H_5)_2$
Michler's ketone	$CO(C_6H_4.NMe_2)_2$
Auramine base	$C(:NH)(C_6H_4.NMe_2)_2$

Since auramine base is colourless and the salts are intensely yellow the latter possibly possess a quinonoid structure, *e. g.*,($C.NH_2$)-($.C_6H_4.NMe_2$)($:C_6H_4:NMe_2Cl$), a hypothesis which receives strong support from an observation of A. Stock, who found that auramine salts may be obtained from Michler's ketone and the hydrochlorides of secondary bases such as methylaniline.

Auramine is now obtained by Sandmeyer's method, which consists in heating a mixture of tetramethyldiaminodiphenylmethane (prepared from formaldehyde and dimethylaniline), sulphur and salt in a stream of ammonia. In this case the thioketone $CS(C_6H_4NMe_2)_2$ is formed as an intermediate product, the sulphur being removed as hydrogen sulphide and replaced by the imino-group.

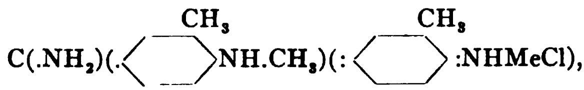
Auramine O appears in commerce as a yellow powder, $C_{17}H_{21}N_3$,-$HCl+H_2O$. It is somewhat sparingly soluble in cold, but more readily in hot water, giving a bright yellow solution. It is also soluble in alcohol. The cold aqueous solution is not changed by hydrochloric acid, but on boiling the liquid is decolourised, with re-formation of ammonium chloride and tetramethyldiaminobenzophenone. On addition of sodium hydroxide, the aqueous solution of auramine yields a white precipitate of the free base. The precipitate dissolves on agitation with ether, and the separated ethereal solution is not fluorescent, but communicates a yellow colour to acetic acid when shaken with it. When treated with zinc and acetic acid, auramine gives an evanescent green colouration. Alkaline reducing agents, such as sodium amalgam or zinc and ammonia, gradually decolourise the alcoholic solution of auramine, and on adding water a colourless reduction-product is precipitated, which when heated with acetic acid yields a deep blue

colour. With strong sulphuric acid it yields a colourless solution, which on dilution with water, becomes yellow in colour.

Auramine dyes textile fibres mordanted with tannin a greenish-yellow which is fairly fast to washing and light, but very sensitive to chlorine; the fibre is decolourised both by alkalies and acids. Auramine has been used to a considerable extent in paper staining and leather dyeing.

Besides the pure grade, Auramine O, other qualities are sometimes met with under the names Auramine I, II, or III; these usually contain a greater or less amount of dextrin.

The **Auramine** G of the Badische Anilin-und-Soda-Fabrik has the constitution



it is prepared by heating dimethyldiaminoditolylmethane with sulphur in a current of ammonia, it is dyed like Auramine O but gives a greener shade of yellow. The liability of the auramines to hydrolysis renders caution necessary in use; the dye-bath should not exceed 160° F. (70°).

Triphenylmethane is the parent hydrocarbon of a large number of dyestuffs the leuco-compounds of which can be considered as di- or tri-parasubstituted hydroxy- or amino-derivatives. The colour varies greatly with the number and nature of the substituting groups which are usually all in the para-position to the parent methane carbon atom, in which position it seems absolutely essential that some of the groups should be situated for the production of a dyestuff. Generally speaking, the introduction of amino-groups has the effect of diminishing the oscillation frequency of the coloured compound to a greater extent than hydroxyl, while substitution of the hydrogen atoms of the amino-groups by alkyl radicals has a further effect in the same direction; this effect is even more marked when radicals of the aromatic series are introduced instead of aliphatic radicals. This is rendered apparent by consideration of the constitutions of pararosolic acid and aurine (orange), pararosaniline (red), Crystal Violet, andt riphenylpararosaniline (blue).

Pararosolic acid $$C\begin{cases} .C_6H_4.OH \\ .C_6H_4.OH \\ :C_6H_4:O \end{cases}$$

Pararosaniline $$C\begin{cases}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ :C_6H_4:NH_2Cl\end{cases}$$

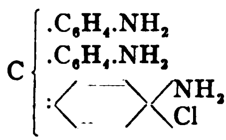
Crystal Violet $$C\begin{cases}.C_6H_4.N(CH_3)_2\\ .C_6H_4.N(CH_3)_2\\ :C_6H_4:N(CH_3)_2Cl\end{cases}$$

Triphenylpararosaniline $$C\begin{cases}.C_6H_4.NH.C_6H_5\\ .C_6H_4.NH.C_6H_5\\ :C_6H_4:NH(C_6H_5)Cl\end{cases}$$

In writing the above formulæ, the generally used paraquinonoid constitutions have been employed though other formulations have been adopted at different times. Thus pararosaniline may also be written as:

$$C\begin{cases}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .C_6H_4.NH_2Cl\end{cases}$$

$$C\begin{cases}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .Cl\end{cases}$$



the last two structures representing the substance as a carbonium salt.

Assuming however the generally received paraquinonoid constitutions represented above, the relationships of the compounds mentioned above to triphenylmethane are easily recognised. By the reduction of pararosaniline a colourless compound, paraleucaniline is produced which is simply triaminotriphenylmethane, for it may be produced from triphenylmethane by the introduction of three nitro-groups and their subsequent reduction to amino-groups in accordance with the scheme,

$$CH(C_6H_5)_3 \rightarrow CH(C_6H_4.NO_2)_3 \rightarrow CH(C_6H_4.NH_2)_3$$

while triphenylmethane may be obtained from paraleucaniline by diazotisation and subsequent boiling with alcohol.

$$CH(C_6H_4.NH_2)_3 \rightarrow CH(C_6H_4.N_2.SO_4H)_3 \rightarrow CH(C_6H_5)_3.$$

While paraleucaniline is a colourless substance, both as free base and as salts, it yields on oxidation in acid solutions the powerfully coloured salts of pararosaniline from which alkalies precipitate a colourless base to which a carbinol structure is usually assigned. The oxidation of the paraleucaniline salt to pararosaniline and the relationship of the latter to a carbinol base may be represented as follows:

$$C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .C_6H_4.NH_2.HCl\\ .H\end{array}\right. \underset{(2H)}{\overset{(O)}{\rightleftarrows}} C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ :C_6H_4:NH_2Cl\end{array}\right. \underset{(HCl)}{\overset{(KOH)}{\rightleftarrows}} C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .OH\end{array}\right.$$

The carbinol bases are colourless and frequently give feebly coloured solutions with cold dilute acid; the colouration of the quinonoid salt develops on standing. It appears probable that the acid first attaches itself to an amino-group, the elements of water being subsequently eliminated.

The anhydride of the carbinol base

$$C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .C_6H_4.NH.\end{array}\right. \quad \text{or more probably} \quad C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ :C_6H_4:NH\end{array}\right.$$

identified by Baeyer with "Homolka's base," is according to his view (*Ber.*, 1905, **38**, 581) an intermediate product in the formation of the carbinol base on treatment of a pararosaniline salt with alkali. The actual anhydride does not appear to have been obtained in a pure condition, a discussion which took place between H. Weil (*Ber.*, 1896, **29**, 1541, 2677; 1900, **33**, 3141) and von Georgievics (*Monatsh.*, 1896, **17**, 7; 1900, **21**, 407; *Ber.*, 1896, **29**, 2015) having led to no definite result; while the products obtained by Baeyer (*Ber.*, 1904, **37**, 2869) gave numbers on analysis lying between those required for the carbinol and anhydro-base. While diamino-fuchsone-imine (Baeyer's name for the anhydro-base of pararosaniline) has not been very definitely isolated, the diphenyldiaminofuchsonephenylimine corresponding to triphenylpararosaniline (Pararosaniline Blue) may be obtained in a

condition giving satisfactory figures on analysis (Baeyer and Villiger, *Ber.*, 1904, **37**, 2871).

$$C\left\{\begin{array}{l}.C_6H_4.NH.C_6H_5\\ .C_6H_4.NH.C_6H_5\\ :C_6H_4:N.C_6H_5\\ \qquad\quad H\ \ Cl\end{array}\right. \qquad HO.C\left\{\begin{array}{l}C._6H_4.NH.C_6H_5\\ .C_6H_4.NH.C_6H_5\\ .C_6H_4.NH.C_6H_5\end{array}\right. \qquad C\left\{\begin{array}{l}.C_6H_4.NH.C_6H_5\\ .C_6H_4.NH.C_6H_5\\ :C_6H_4:N.C_6H_5\end{array}\right.$$

Pararosaniline blue. Carbinol base.[1] Diphenylaminofuchsone-phenylimine.

The relationships between pararosaniline and Crystal Violet and pararosaniline blue are evident since the two latter compounds may be respectively obtained by the methylation and phenylation of pararosaniline.

Pararosolic acid may be obtained from pararosaniline by the action of nitrous acid, while the converse change may be effected by heating *p*-rosolic acid with ammonia solution to 200° under pressure. A less energetic treatment with ammonia effects partial replacement of the hydroxyl groups with the production of red corallin or peonin.

Pararosolic acid may also be reduced to a leuco-compound, trihydroxytriphenylmethane, similarly capable of oxidation to the original dyestuff

$$C\left\{\begin{array}{l}.C_6H_4.OH\\ .C_6H_4.OH\\ .C_6H_4.OH\\ .H\end{array}\right. \quad \begin{array}{c}(O)\\ \longrightarrow\\ \longleftarrow\\ (2H)\end{array} \quad C\left\{\begin{array}{l}.C_6H_4.OH\\ .C_6H_4.OH\\ :C_6H_4:O\end{array}\right.$$

Besides possessing phenolic properties, Aurine (*p*-rosolic acid) combines with acids; reference will be made to the generally basic character of triphenylcarbinol and its derivatives.

The colour and dyeing properties of triphenylmethane dyestuffs are conditioned not only by whether the auxochromic amino-groups are unsubstituted, alkylated or phenylated, but also by the number of

[1] It may be noted that Weil (*Ber.*, 1895, **28**, 205) has suggested an alternative formula for the carbinol bases, thus for pararosaniline he gives

$$C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ .C_6H_4.NH_2\end{array}\right.\ \ O$$

benzene nuclei in which substitution has been effected. Thus the parent substance fuchsone-imine

$$C\begin{cases}.C_6H_5\\.C_6H_5\\:C_6H_4:NH_2Cl\end{cases}\qquad\qquad C\begin{cases}.C_6H_4\\.C_6H_4.NH_2\\:C_6H_4:NH_2Cl\end{cases}$$

Fuchsone-imine salt. Doebner's violet.

is coloured and gives reddish-orange salts only capable of dyeing cotton mordanted with tannin. One additional amino-group leads to the reddish-violet salts of Doebner's Violet, while yet another amino-group is contained in pararosaniline.

A comparison may also be instituted between the methylated amino-fuchsone-imines; thus malachite green contains one dimethylamino-group less than crystal violet.

$$C\begin{cases}.C_6H_5\\.C_6H_4.(NCH_3)_2\\:C_6H_4:N(CH_3)_2Cl\end{cases}\qquad C\begin{cases}.C_6H_4.N(CH_3)_2\\.C_6H_4.N(CH_3)_2\\:C_6H_4:N(CH_3)_2Cl\end{cases}\qquad C\begin{cases}.C_6H_4.N(CH_3)_3Cl\\.C_6H_4.N(CH_3)_2\\:C_6H_4:N(CH_3)_2Cl\end{cases}$$

Malachite green. Crystal violet. Methyl green.

The "auxochromic" effect of this dimethylamino-group is very marked,[1] for if it be converted into an ammonium group by the addition of methyl chloride, a green colouring matter is once more obtained.

Malachite Green is obtained by the oxidation of the tetramethyl-diaminotriphenylmethane which results from the condensation of benzaldehyde with dimethylaniline, substituted benzaldehydes giving derivatives of Malachite green which generally speaking show only minor differences of shade when the substituents are not such as can be considered as auxochromic in their action. It is different however in the case of the hydroxybenzaldehydes, for with this compound the members of the Patent blue (greenish-blue) group can be prepared.

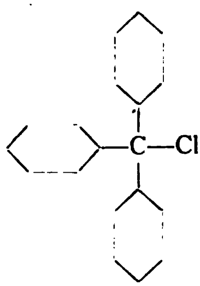
Most of the dyestuffs of the triphenylmethane series are basic colouring matters, though in many cases they are used as acid dyestuffs, sulphonic groups being introduced into the molecule. This sulphonation which does not effect any radical alteration in colour is often resorted to in order to render a dyestuff water-soluble.

The cause of the colour (selective absorption in the visible spectrum)

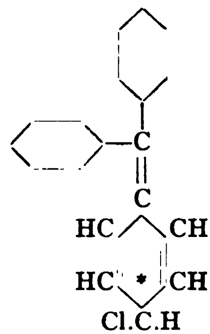
[1] For a discussion of the effect of auxochromic groups, reference may be made to Hugo Kauffmann, "*Die Auxochrome*," *Ahrens' Sammlung*, 1907, 12.

of these compounds has caused considerable discussion; it is probably connected with their quinonoid constitution.[1]

It is a noteworthy fact that triphenylmethyl chloride dissolves in concentrated sulphuric acid with evolution of hydrogen chloride giving a golden yellow solution from which on large dilution with water the colourless triphenylcarbinol is precipitated (Norris and Sanders, *Amer. Chem. J.*, 1901, **25**, 54; F. Kehrmann and F. Wentzel, *Ber.*, 1901, **34**, 3815); moreover, a number of coloured salts can be isolated from triphenylcarbinol, and Kehrmann and Wentzel assume in these a quinonoid constitution:



Colourless.



Coloured.

Gomberg and Cone hold much the same view (*Ber.*, 1907, **40**, 1847; 1909, **42**, 406; *Annalen*, 1909, **370**, 145) stating that triphenylchloromethane and all analogous compounds exist in two tautomeric forms, the colourless having a benzenoid structure while a quinonoid constitution is to be given to those which are coloured. According to them, the carbon atom marked * assumes basic properties and the substances are to be looked on as real "quinocarbonium salts." (Compare Flürscheim, *Trans. Chem. Soc.*, 1910, **97**, 91.)

Until recently the coloured salts isolated in a condition fit for analysis have been double metallic chlorides, but Gomberg and Cone show that in many cases coloured perchlorates containing only 1 molecule of acid per molecule of base can be prepared. A similar line of research is also being pursued by K. A. Hofmann and his co-workers who have isolated the coloured mono-perchlorates of triphenylcarbinol,

[1] See H. E. Armstrong, *Proc. Chem. Soc.*, 1888, **4**, 27; 1892, **8**, 101, 103, 143, 189, 194; W. N. Hartley, *Proc. Chem. Soc.*, 1892, **8**, 188; Nietzki, *Organische Farbstoffe*, and many later papers by Baly, Green, Hantzsch, Hewitt, Kaufmann, etc.

phenolphthalein and dibenzylideneacetone, the diperchlorate of fluorescein (*Ber.*, 1909, **42**, 4856) as well as the monoperchlorates of aurin and trianisylcarbinol (*Ber.*, 1910, **43**, 183).

Evidently then triphenylcarbinol is capable of yielding a carbon and hydrogen complex to which weak basic function must be attributed, the introduction of amino- or alkylamino-groups in the para-position to the methane carbon atom, and, in a lesser degree hydroxyl or alkyloxyl groups increases considerably the basic properties so that in the case of pararosaniline and Crystal Violet, salts are encountered which show no sign of hydrolytic dissociation in aqueous solution (Miolati, *Ber.*, 1890, **23**, 1788; 1895, **28**, 1696; Hantzsch and Osswald, *Ber.*, 1900, **33**, 278).

From such solutions alkalies yield precipitates of carbinol bases, colourless, insoluble in water, soluble in organic liquids and without alkaline reaction, evidently differing in constitution from the salts from which they are obtained; this in fact furnishes a most important argument for the relationship usually assumed to exist between coloured quinonoid salts and colourless carbinol bases.

DIAMINOTRIPHENYLMETHANE DYESTUFFS.

These triphenylmethane colouring matters, containing two para aminated aromatic nuclei, are usually prepared from an aromatic aldehyde and two molecules of an aromatic amine (usually tertiary) the resulting leuco-compound being subsequently oxidised.

Doebner's Violet (aminofuchsone-imonium chloride) is the typical substance of this group but is of no technical importance. The simplest dyestuff of the series which occurs in commerce is *Malachite Green*, the leuco-compound of which is produced by the condensation of benzaldehyde with two molecules of dimethylaniline.

$$C_6H_5.CHO + 2C_6H_5.N(CH_3)_2 = H_2O + C_6H_5.CH(C_6H_4.NMe_2)_2$$

Subsequent oxidation in acid solution gives the dyestuff

$$C_6H_5.CH\begin{cases} :C_6H_4.N(CH_3)_2 \\ .C_6H_4.N(CH_3)_2HCl + O = \end{cases}$$

$$H_2O + C_6H_5.C\begin{cases} .C_6H_4.N(CH_3)_2 \\ :C_6H_4:N(CH_3)_2Cl \end{cases}$$

The process depending on the direct condensation of benzotrichloride with a secondary base is of no technical importance.

In preparing acid dyestuffs of this group the dimethylaniline is replaced by bases such as ethyl-benzyl-aniline, the benzyl group being readily accessible to sulphonation. The preparation of the acid of *Light Green SF.* is easily followed by means of the following scheme:

$$C_6H_5.CHO + 2C_6H_5.N\left\{\begin{array}{l}.C_2H_5\\ .CH_2.C_6H_5\end{array}\right. \rightarrow$$

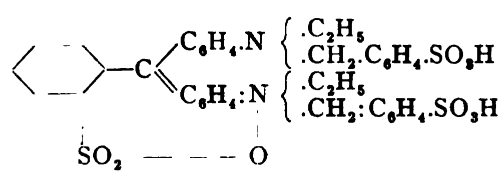
$$C_6H_5.CH\left(.C_6H_4.N\left\{\begin{array}{l}.C_2H_5\\ .CH_2.C_6H_5\end{array}\right.\right)_2 \rightarrow$$

$$C_6H_4\left\{\begin{array}{l}.CH\left(.C_6H_4.N\left\{\begin{array}{l}.C_2H_5\\ .CH_2.C_6H_4.SO_3H\end{array}\right.\right)_2\\ .SO_3H\end{array}\right. \rightarrow$$

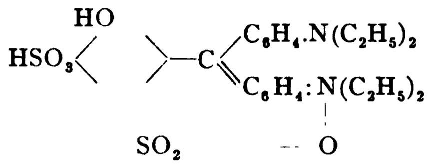
$$C_6H_4\left\{\begin{array}{l}.C(OH)\left(.C_6H_4.N\left\{\begin{array}{l}.C_2H_5\\ .CH_2.C_6H_4.SO_3H\end{array}\right.\right)_2\\ .SO_3H\end{array}\right. \rightarrow$$

$$\begin{array}{l}C_6H_4.C\left\{\begin{array}{l}.C_6H_4.N\left\{\begin{array}{l}.C_2H_5\\ .CH_2.C_6H_4.SO_3H\end{array}\right.\\ :C_6H_4:N\left\{\begin{array}{l}.C_2H_5\\ .CH_2.C_6H_4.SO_3H\end{array}\right.\end{array}\right.\\ SO_3 \text{———————} O\end{array}$$

Dyestuffs obtained in this manner are not very fast to alkali since they are easily hydrolysed to salts of the colourless carbinol-trisulphonic acid; this fault is not met with when a sulphonic acid group in the non-aminated nucleus stands in the ortho-position to the methane carbon atom. Examples may be given of *Erioglaucine*, obtained from benzaldehyde-*o*-sulphonic acid and ethylbenzylaniline sulphonic acid (sulphonated in the benzyl group), and *Patent Blue*, which is prepared from *m*-hydroxybenzaldehyde and diethylaniline, the leuco-compound being subsequently sulphonated and oxidised.



Erioglaucine.



Patent blue.
(Both given as the free acids.)

Malachite Green, or **Benzaldehyde Green,**[1] is obtained by the reaction of dimethyl-aniline on benzaldehyde, whereby tetramethyl-paradiamino-triphenyl-methane is produced, thus:

$$C_6H_5.CHO+2C_6H_5.NMe_2=H_2O+C_6H_5.CH(C_6H_4NMe_2)_2.$$

The hydrochloric acid solution of the product is oxidised by peroxide of lead at 60°–80°, preferably with addition of a little chloranil. The lead is removed by sodium sulphate, and the filtrate treated with common salt and zinc chloride, when the double zinc compound is precipitated.

The *double zinc chloride* of tetramethyl-diamino-triphenyl-carbinol contains $3C_{23}H_{24}N_2,HCl+2ZnCl_2+2H_2O$. It forms brass-yellow prisms, with a yellowish-green reflection.

The *double iron chloride* (ferrous) also occurs in commerce as an inferior quality of benzaldehyde green.

The *oxalate*, $C_{23}H_{26}N_2,C_2O_4$, forms scales having a green metallic reflection.

All the commercial forms of benzaldehyde green dissolve easily in water and alcohol. They are also soluble in amyl alcohol, which character distinguishes them from methyl green (and its allies).

The *free base* of benzaldehyde green is obtained as a green precipitate on adding an alkali to the solution of one of its salts. The precipitate is soluble in ether and petroleum spirit, and after crystallisation from the latter solvent forms colourless needles, which melt at 126°–130°.

The base of Malachite Green combines with both 1 and 2 molecules of picric acid to form insoluble picrates.

The solutions of benzaldehyde green are bluish-green. By concentrated hydrochloric acid they are changed to orange-yellow, but the green colour is restored by dilution. Hypochlorites decolourise the solution, and stannous chloride forms a green precipitate.

[1] Also known as *Malachite Green B, Benzal Green, New Victoria Green, New Green, Solid Green, Solid Green, O, Diamond Green, Dragon Green, Benzoyl Green,* and *Fast Green.*

Benzaldehyde green may be detected on fibres dyed with it by the orange colouration with hydrochloric acid, restored to green by washing, and by the decolourisation produced by ammonia, soda, or soap. From methyl green it is distinguished by not turning violet when heated.

Ethyl Green (*Brilliant Green, Malachite Green G, New Victoria Green, Emerald Green, Fast Green J, Diamond Green G, Smaragdgreen* and *Solid Green J, JJO*) is homologous with Malachite Green, and consists either of the sulphate or zinc chloride compound of tetraethyl-diamino-triphenyl-carbinol. It is prepared in a manner similar to that of malachite green, diethylaniline being substituted for the dimethylaniline. The dyeing power of brilliant green is not so intense as that of malachite green, and its shade is yellower.

Victoria Green 3 B (*New Fast Green 3 B, and New Solid Green BB*) is a chlorinated malachite green, being obtained from dichlorobenzaldehyde and dimethyl-aniline. It occurs as the hydrochloride (or zinc chloride compound) of tetramethyl-diamino-dichloro-triphenylcarbinol. Its general properties are, almost the same as those of malachite green, but it dyes a bluer shade than the latter.

Helvetia Green (*Acid Green*) is the type of the sulphonated aniline greens, the properties of which have already been described. It differs from benzaldehyde green by giving no precipitate with sodium hydroxide in dilute solutions, though strong solutions produce a white precipitate. On the fibre, acid green closely simulates benzaldehyde green, but it is turned greenish-yellow by hydrochloric acid, the liquid itself becoming yellow; whereas fibres dyed with benzaldehyde green become bright orange, and give up very little colour to hydrochloric acid. In each case the original green colour is restored by washing with water. From methyl green, Helvetia Green is distinguished by the fibres not becoming violet when heated.

Light Green SF (bluish) and **Light Green SF** (yellow) are disulphonic acid derivatives of the benzaldehyde group. They are prepared by heating benzaldehyde with benzylmethyl- (or ethyl) aniline and sulphonating the products so obtained by means of fuming sulphuric acid; subsequent oxidation gives the dyestuffs. The yellow shade dyestuff is also met with under the names *Acid Green SOF, Acid Green D, Acid Green JJ*, and *Light Green S*, while the blue shade is sometimes called *Acid Green* and *Acid Green M*.

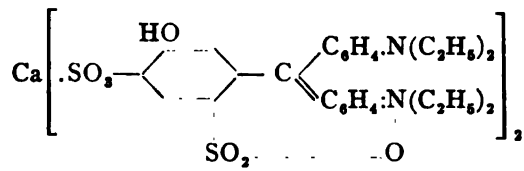
According to a recent patent (J. R. Geigy, German pat. 204,034)

dyestuffs quite fast to alkali are produced when 2 : 6-dichlorobenzaldehyde or its 3-nitro-derivative are condensed with ethyl- (or methyl) benzylaniline sulphonic acid and the leuco-compound oxidised. The chlorine atoms only produce a slight blueness of shade.

Erioglaucine is a dyestuff of pure blue shade produced by the condensation of benzaldehyde-*o*-sulphonic acid with ethyl-benzylaniline, the benzyl groups are then sulphonated and the resulting leuco-compound oxidised.

Patent Blue.—Different marks of dyestuffs of this class are met with in commerce (*A*, *N*, *V*, *superfine*, etc.). The original discovery that *m*-hydroxybenzaldehyde when condensed with alkyl derivatives of aniline and the resulting leuco-compound sulphonated and oxidised gave rise to valuable greenish-blue dyestuffs, was made by Herrmann in 1888 in the factory of Meister, Lucius and Brüning (German patent 46,384).
this class depend on the condensation of *m*-nitro- or *m*-amino-benzaldehyde with dialkylated anilines, in the former case reduction of the nitro- to an amino-group, replacement of the latter by hydroxyl; sulphonation, and oxidation of the calcium or magnesium salt of the leuco-sulphonic acid.

Patent Blue V has been studied by Erdmann from a scientific standpoint (*Annalen*, 1897, **294**, 376); his results show that it is a calcium salt of the constitution



The commercial dye forms a dark blue crystalline powder readily soluble in water with a greenish-blue colour; it is somewhat soluble in water but practically insoluble in solvents such as ether and benzene. Concentrated sulphuric acid dissolves it with difficulty, giving an olive-yellow solution; with dilute sulphuric acid an olive-green solution is obtained. The aqueous solution becomes bluer on addition of sodium hydroxide or ammonia, while stannous chloride produces partial precipitation and gives a yellow-green colouration. Solutions are readily reduced by zinc dust in presence of ammonia or acetic acid, the filtrates being colourless.

Patent Blue A is obtained by using ethylbenzylaniline in place of diethylaniline, and *Cyanol* or Acid Blue 6 G by using ethyl-*o*-toluidine as base. Oxidation of members of the Patent Blue Group with ferric chloride gives rise to dyestuffs known as *Cyanines*.

Azo-green is a mordant dyestuff obtained by diazotising *m*-aminotetramethyldiaminotriphenylmethane and coupling with salicylic acid, the leuco-compound then being oxidised. In solution the dye is turned to a dirty yellow by concentrated sulphuric and hydrochloric acids; when dyed on the fibre with a chromium mordant, these reagents produce a light brown.

Diaminotriphenylmethane derivatives obtained by the condensation of tetramethyldiaminobenzhydrol will be referred to under the triaminotriphenylmethane dyestuffs.

TRIAMINOTRIPHENYLMETHANE DYESTUFFS.

Magenta was one of the earliest dyestuffs to be discovered and is produced by the oxidation of *aniline for red*. Benzene containing toluene when nitrated yields a mixture of nitrobenzene and *o*- and *p*-nitrotoluenes; the corresponding amino-bases are produced by their reduction and when such a mixture is oxidised a red dye is produced. As will be noted below, a base containing an amino-group in the *para*-position to a methyl group is essential for the production of dyestuffs of the triaminotriphenylmethane group by this process. We now pass to the general methods of preparation.

1. Oxidation of a mixture containing 1 molecular proportion of *p*-toluidine with 2 molecular proportions of amines with the para-position free:

$$C\begin{cases}.C_6H_4.NH_2\\.H\\.H\\.H\end{cases}+C_6H_5.NH_2+C_6H_4\begin{cases}(1).NH_2\\(2).CH_3\end{cases}+3O=$$

$$2\,H_2O+C\begin{cases}.C_6H_4.NH_2\\.C_6H_4.NH_2\\.C_6H_3\begin{cases}.NH_2\\.CH_3\end{cases}\\.OH\end{cases}$$

This is the chief change taking place in the magenta melt; if *p*-toluidine be heated with 2 molecular proportions of *o*-toluidine, the

corresponding ditolylphenyl dye is produced, while *p*-toluidine and aniline yield pararosaniline.

2. Replacement of hydroxyl by the amino-group in aurin by heating under pressure with ammonia.

3. The *new fuchsin process* of Meister, Lucius and Brüning. Formaldehyde and aniline unite to form anhydroformaldehydeaniline, which when heated with aniline and aniline hydrochloride yields diaminodiphenylmethane.

$$C_6H_5.N:CH_2+C_6H_5.NH_2=CH_2(C_6H_4.NH_2)_2.$$

The latter substance heated with aniline hydrochloride in presence of an oxidising agent gives pararosaniline.

$$CH_2(C_6H_4.NH_2)_2+C_6H_5.NH_2,HCl+2O=2H_2O+C\begin{cases}.C_6H_4.NH_2\\.C_6H_4.NH_2\\:C_6H_4:NH_2Cl\end{cases}.$$

This method is capable of furnishing a considerable variety of dyestuffs since other bases than aniline may be used; thus using *o*-toluidine, *New Fuchsine* is produced.

4. The hydrogen atoms of the amino-groups of pararosaniline and its homologues may be replaced by alkyl groups. This was formerly effected by the action of alkyl halides. (See Method 6.)

5. Aromatic radicals may be also used in replacing the hydrogen atoms of the amino-groups, the dyestuff being heated with an amino-base (and a little benzoic acid). The action is comparable to the formation of diphenylamine by heating aniline with its hydrochloride.

$$C\begin{cases}.C_6H_4.NH_2\\.C_6H_4.NH_2\\:C_6H_4:NH_2Cl\end{cases}+3C_6H_5.NH_2=3NH_3+C\begin{cases}.C_6H_4.NH.C_6H_5\\.C_6H_4.NH.C_6H_5\\:C_6H_4:NH(C_6H_5)Cl\end{cases}$$

A similar dyestuff is produced by heating oxalic acid with diphenylamine.

$$C_2O_4H_2+3C_6H_5.NH.C_6H_5=CO+2H_2O+HO.C(C_6H_4.NH.C_6H_5)_3.$$

On account of their very sparing solubility in water, these compounds are usually sulphonated and employed as acid dyestuffs.

6. A methylated pararosaniline (*Methyl Violet*) is obtained by the oxidation of dimethylaniline. The reaction is explained by supposing that one methyl group is oxidised to formaldehyde which then con-

denses with 1 molecule of monomethylaniline and 2 molecules of dimethylaniline to form a pentamethylpararosaniline.

$$CH_2O + C_6H_5.NH.CH_3 + 2C_6H_5.N(CH_3)_2 + 2O = 2H_2O + HO.C\begin{cases} .C_6H_4.NH.CH_3 \\ .C_6H_4.N(CH_3)_2 \\ .C_6H_4.N(CH_3)_2 \end{cases}$$

7. Alkylated dyestuffs are produced by the action of carbonyl chloride on tertiary aromatic bases. (Phosgene process of Kern and Caro, 1883.) With dimethylaniline, Michler's ketone (tetramethyldiaminobenzophenone) is first produced which by the further action of carbonyl chloride or of phosphorous oxychloride is converted into the keto-chloride

$$CCl_2[C_6H_4.N(CH_3)_2]_2$$

With a third molecule of dimethylaniline condensation takes place, Crystal Violet being produced.

$$CCl_2[C_6H_4.N(CH_3)_2]_2 + C_6H_5.N(CH_3)_2 = HCl + C\begin{cases} .C_6H_4.N(CH_3)_2 \\ .C_6H_4.N(CH_3)_2 \\ :C_6H_4:N(CH_3)_2Cl \end{cases}$$

8. By reduction of Michler's ketone or oxidation of tetramethyldiaminodiphenylmethane the corresponding secondary alcohol (Michler's hydrol) may be obtained which condenses with a large number of amines, phenols, and carboxylic acids to form leuco-compounds of tri- and di-aminotriphenylmethane dyestuffs.

Thus the leuco-compounds of

$$C\begin{cases} .C_6H_4N(CH_3)_2 \\ .C_6H_4.N(CH_3)_2 \\ :(1)C_{10}H_6(4):NH(C_2H_5)Cl \end{cases}$$

Victoria Blue R.

$$C\begin{cases} :(1)C_6H_4(4):N(CH_3)_2Cl \\ .(1)C_6H_4(4).N(CH_3)_2 \\ .(1)C_{10}H_5\begin{cases} (3).COOH \\ (4).OH \end{cases} \end{cases}$$

Chrome Blue.

are produced by its condensation with ethyl-α-naphthylamine and α-hydroxynaphthoic acid respectively.

Magenta is a salt of rosaniline, with which a certain amount of the

corresponding pararosaniline salt is usually mixed. The oxidation of the "aniline oil for red" (aniline, *o*- and *p*-toluidines) may be effected by means of arsenic acid, mercuric nitrate or nitrobenzene, in the last case ferrous chloride being used as an oxygen carrier. Arsenic acid is still occasionally employed but generally the nitrobenzene process is used on account of the risk of contamination with arsenic. Details of the preparation of magenta by this process on the small scale are given by J. C. Cain and J. F. Thorpe in their very useful work *The Synthetic Dyestuffs and Intermediate Products*, p. 244, where references relating to the manufacture of the dye will also be found.

Formerly the nitrate and acetate were to be met with commercially but now little except the chloride is produced; other names by which magenta is or has been known are *Fuchsine*, *Aniline-red*, *Azaleine*, *Rubine*, *Roseine*, *Solferino*, *Erythrobenzene*, etc.

Magenta usually occurs in beetle-green crystals or as a dark-green crystalline powder. It dissolves in water giving a magnificent crimson colour without fluorescence. The dilute aqueous and alcoholic solutions of magenta exhibit characteristic absorption-spectra, having a well-defined band between the Fraunhöfer lines D and E.

Solutions of magenta dye silk and wool without a mordant. The colouring matter is partially removed by boiling water, while soap removes it completely.

Alkali hydroxides, ammonia, barium, calcium and magnesium hydroxides decompose solutions of magenta, free rosaniline being precipitated in a crystalline and nearly colourless state. If magnesium oxide be used, and the operation conducted in a boiling hot liquid, so that some of the liberated rosaniline may remain in solution, and the liquid be then filtered out of contact with air, a colourless filtrate is obtained. On passing carbon dioxide, or the air exhaled from the lungs, through this colourless solution of rosaniline, a crimson colouration is produced, owing to the formation of rosaniline carbonate. The reaction constitutes a delicate test for carbon dioxide.[1]

If a solution of magenta be treated with excess of soda or ammonia and then agitated with ether, the liberated rosaniline dissolves. The separated ethereal solution is colourless, but dyes silk a fine crimson, and on shaking with dilute acetic acid yields a crimson solution.

Excess of strong hydrochloric acid turns magenta solutions yellow

[1] A solution of magenta in glacial acetic acid is a delicate test for nitrous acid and nitrites, which change the colour first to violet, then through blue, green and yellow to orange. Nitric acid does not show this behaviour.

or brown, owing to the formation of a triacid salt, which is decomposed on copious dilution, or on adding a solution of sodium acetate, with restoration of the original crimson colour.

Reducing agents, such as zinc and acetic or hydrochloric acid, stannous chloride, sulphurous acid,[1] etc., decolourise solutions of magenta forming colourless salts of leucaniline, $C_{20}H_{21}N_3$. This base differs from the products resulting from the reduction of safranine, magdala-red, and certain other colouring matters, in not being reconverted into rosaniline by atmospheric oxygen. On the other hand, oxidation of leucaniline to rosaniline can be effected by manganese dioxide, chloranil, and similar agents.

Strong oxidising agents, such as permanganates, hypochlorites, and chlorine, decolourise solutions of magenta. Oxidising agents of moderate power produce new colouring matters, a yellowish-red product known as *aniline-scarlet* being formed by the action of hydrogen peroxide or lead nitrate. Chromic acid acts on magenta, giving a brown colouring matter.

Aldehyde and an alcoholic solution of shellac convert magenta into blue colouring matters.

Solid magenta dissolves in strong sulphuric acid with yellowish-brown colour, becoming violet-red on dilution with water.

Detection of Magenta.—When perfectly pure, magenta is not poisonous, but as occurring in commerce it frequently contains arsenic, and hence is unsuitable for colouring confectionery, syrups, wines, etc. Its use for such purposes is absolutely forbidden in some countries.

The detection of magenta is based on the foregoing tests, but in order to apply these satisfactorily it is usually necessary to isolate the colouring matter more or less perfectly.

Examination of Commercial Magenta.—Pure magenta consists simply of the hydrochloride or other salt of rosaniline, mixed with more or less of the corresponding compound of pararosaniline. The commercial product generally contains, in addition, more or less water, mineral impurities, resinous substances, and, if prepared by the arsenic acid process, a notable quantity of arsenic. Besides these impurities, actual adulterants are sometimes present, the most usual being sugar, starch, dextrin, sodium sulphate, and occasionally bronze powder.

[1] Fuchsine-sulphurous acid, prepared by passing sulphurous acid gas into a dilute solution of magenta until the crimson colour has changed to a pale yellow, is a very delicate test for aldehydes and some of their derivatives, as these give an intense violet-red colour with it.

Magenta of good quality being generally well crystallized, powdered or imperfectly crystalline specimens are always open to suspicion.

The blue shades of magenta are generally the purest. The yellow shades, if made by the arsenic acid process, usually contain Phosphine; magenta made by the nitrobenzene process contains no Phosphine (see page 263).

A solution of pure magenta is entirely decolourised by sulphurous acid, while impure samples are turned yellow or brown; or the hot aqueous solution of the sample may be treated with hydrochloric acid, and zinc-dust then gradually added in small quantities at a time, till the red colour is destroyed. With pure magenta the reduced liquid will be colourless, but if *chrysaniline* be present it will have a yellow tint.

Arsenic is sometimes present in commercial magenta in considerable proportion, as much as 6.5% having been met with. It may be detected by Marsh 's test. For its estimation, the acidified solution may be treated with bromine water, excess of ammonia added, the liquid filtered if necessary, and magnesia mixture then added. A precipitate of the ammonio-magnesium arseniate, deposited in streaks in the track of the glass rod used for stirring, will be gradually formed if arsenic be present. The arseniate may be distinguished from the similar phosphate by washing the precipitate or streaks with water, and adding silver nitrate, when the arseniate will be turned brown, or the phosphate yellow.

The detection of other impurities and adulterants of magenta will be described in the section on the "Examination of Commercial Colouring Matters."

Acid Magenta, called also *Magenta S* and *Rubine S*,[1] is obtained by heating ordinary magenta with fuming sulphuric acid or chlorosulphonic acid, SO_3HCl. The product is poured into water, neutralized with milk of lime, the solution filtered from the calcium sulphate, and the filtrate decomposed by sodium carbonate. The calcium carbonate is filtered off and the filtrate evaporated to dryness. Acid Magenta occurs in grains or powder of a green colour and metallic lustre. It dissolves readily in water, forming a bluish-red solution, which is nearly decolourised by alkalies without a precipitate being formed, and nothing is yielded to ether. Dilute acids, even carbonic acid, restore the

[1] Impure forms of acid magenta are to be met with under the names of *Maroon S*, *Grenat S*, *Acid Cerise*, *Cardinal Red S*, *Acid Maroon*, etc.

colour, which is not materially altered by a considerable excess. In strong sulphuric acid, the solid dye dissolves with yellow colour, becoming gradually red on dilution.

According to C. Blarez, all red coal-tar dyes except acid magenta, and also all red vegetable colouring matters, are completely decolourised when their aqueous solutions are slightly acidified with tartaric acid and digested with lead peroxide.

In its behaviour with reducing agents and acetone, acid magenta reacts like the basic dye.

Acid magenta is employed for colouring red wines. Being insoluble in ether, it may be distinguished from ordinary magenta.

Acid magenta has only about half the dyeing power of ordinary magenta, but can be dyed from strongly acid baths, and hence is conveniently employed in conjunction with acid yellow, indigo-carmine, etc.

On the fibre, acid magenta is unaffected in colour by a mixture of equal volumes of hydrochloric acid and water, whereas ordinary magenta is turned yellow or brown. The reagent dissolves some of the acid magenta, and acquires a cherry-red colour.

Aniline Blues.

As stated already the phenylated derivatives of rosaniline and pararosaniline dye bluer shades than the unsubstituted bases, and this in proportion to the number of hydrogen atoms replaced by phenyl, C_6H_5. Thus the colouring matter known as *Regina Violet* is chiefly a salt of diphenyl-rosaniline, while the various commercial aniline blues are mostly triphenylated derivatives; and Benedikt states that hexaphenyl-rosaniline yields a purer blue than any other colouring matter known.

Besides a few aniline colours of a somewhat different constitution, there occur in commerce two parallel series of blue dyes, which are triphenylated derivatives of pararosaniline and rosaniline respectively.

The parallel compounds from para-rosaniline and rosaniline present a close analytical and general resemblance. In addition, the phenylated products from commercial rosaniline invariably contain more or less of their lower homologues (from para-rosaniline), and hence there is no sharp distinction between the 2 series of dyes.

Diphenylamine Blue or para-rosaniline blue[1] is the hydrochloride

[1] Also known as *Bavarian Blue* spirit soluble.

of triphenyl-pararosaniline, and contains $C_{19}H_{14}(C_6H_5)_3N_3.HCl$. It is prepared by heating diphenylamine, $(C_6H_5)_2$: NH, at 120°–130° with oxalic acid. The excess of oxalic acid is removed by washing with water and unaltered diphenylamine by boiling with benzene, the residue being then converted into the hydrochloride. The commercial dye forms a brownish powder, having an odour resembling that of diphenylamine. It is insoluble in water and only sparingly soluble in cold alcohol, but dissolves more readily on heating. The solution is turned greenish by hydrochloric acid. A 2% solution of the colouring matter in methylated spirit is employed to produce light and very pure shades of blue on silk. Diphenylamine blue dissolves in strong sulphuric acid with brownish-yellow colour, a blue precipitate being produced on dilution.

The colouring matter known as *Azuline* or *Azurine* is an impure hydrochloride of triphenyl-pararosaniline.

Colouring matters known as *Methyl Blue* and *Ethyl Blue* are obtainable by the action of methyl or ethyl chloride on diphenylamine blue or by heating methyl- or ethyl-diphenylamine with oxalic acid. The products dye silk a still purer blue than that produced by diphenylamine blue. One of the purest blues is obtained by treating methyldiphenylamine at 100° with chloranil (tetrachlorquinone), $C_6Cl_4O_2$, and then further heating to 130°. The product is reduced to powder, washed with hydrochloric acid, dissolved in alcohol, and precipitated by water.

Rosaniline Blue, also called *Spirit Blue, Aniline Blue, Opal Blue, Gentian Blue* 6 *B, Fine Blue, Hessian Blue,* is a salt of triphenylrosaniline, containing more or less of the corresponding salt of triphenylpararosaniline. To prepare it, rosaniline (prepared by precipitating a solution of the purest bluish magenta with ammonia or lime) is heated to about 180° with 10 times its weight of aniline and some benzoic acid. The excess of aniline, together with the ammonia formed in the action, distils over. The product is neutralised with dilute hydrochloric acid, when aniline hydrochloride dissolves and the salt of the new base remains insoluble. This is washed first with dilute hydrochloric acid and then with water, and dried and powdered.

Sulphonated Aniline Blues.

Diphenylamine Blue and Spirit Blue being insoluble in water, their practical application is attended with some inconvenience, to obviate

which they are frequently sulphonated, with production of soluble colouring matters known as *Soluble Blue, Water Blue, Water Blue 6 B, China Blue, London Blue, Cotton Blue, Opal Blue, Marine Blue.*[1]

The greater the number of SO_3H groups that are introduced into triphenylrosaniline or its homologues, the more readily soluble the products become, but their fastness to light and air, soap, and alkalies decreases in the same proportion. Hence the higher sulphonic acids, such as triphenyl-rosaniline tetrasulphonic acid, are never prepared.

The sulphonated aniline blues are prepared by heating Diphenylamine Blue and Spirit Blue with concentrated sulphuric acid, the extent of the sulphonation depending on the proportion of acid used and the temperature employed. A soluble diphenylamine blue may be prepared directly by heating diphenylamine-sulphonic acid with oxalic acid, instead of sulphonating the previously prepared triphenylpararosaniline.

Triphenylrosaniline-monosulphonic acid has the formula $C_{20}H_{15}(SO_3H)(C_6H_5)_3N_3$, and is formed by dissolving Spirit Blue in strong sulphuric acid and heating the solution at 30°–35° for 5 or 6 hours. On pouring the resultant brownish-yellow solution into water, the sulphonic acid is obtained as a bulky blue precipitate, which after being dried at 100° forms small grains having a metallic lustre. Its alkali-metal salts are soluble in water, but those formed with the heavy metals and alkaline-earth metals are insoluble or nearly so. By digesting the washed sulphonic acid in a quantity of sodium hydroxide solution somewhat less than that required to combine with it, and filtering, a solution of the sodium salt is obtained, from which the solid compound may be prepared by saturating the liquid with common salt, or evaporating it to dryness with addition of a little ammonium carbonate.

Sodium triphenylrosaniline-monosulphonate forms the commercial dyestuff known as *Nicholson's Blue, Alkali Blue, Soluble Blue* or *Fast Blue*. It occurs in lumps or powder of a greyish, brownish or dull blue colour. It dissolves readily in hot water, with light brown or bluish colour, which becomes deep blue on adding acetic acid, and on boiling the acidified liquid the free sulphonic acid separates as a blue precipitate. Hydrochloric acid produces the same reaction in the cold, and on filtering a colourless liquid is obtained, unless a di- or trisul-

[1] Also known as *Cotton Blue 3 B, Bleu de Lyon, Water Blue B, BS, Blue BVSI, Blackley Blue, Pure Blue, Water Blue OO.*

phonate be present. Sodium hydroxide turns the solution of Soluble Blue reddish-violet, the colour changing on boiling to reddish-brown. Excess of ammonia decolourises the solution. Calcium chloride and stannous chloride produce blue precipitates. Soluble Blue dissolves in strong sulphuric acid with a fine brownish-red colour, becoming blue on dilution with water.

If wool be immersed in a hot solution of Alkali Blue, preferably containing borax, sodium silicate, sodium carbonate, or ammonia, the nearly colourless salt is taken up by the fibre and cannot be removed by washing with water; but on subsequently immersing the fibre in dilute sulphuric acid the blue colour is developed.

Cold alcohol readily removes the colour from wool or silk dyed with Alkali Blue. Sodium hydroxide turns the fibre a yellowish-brown, while ammonia immediately destroys the colour. Hydrochloric acid nearly decolourises the fibre, and an acid solution of stannous chloride destroys it gradually.

Commercial Alkali Blue is liable to contain various impurities and adulterations. It should dissolve without residue in about 5 parts of hot water. Sugar, starch, and dextrin are sometimes added, and a considerable proportion of sodium carbonate, sulphate, or chloride is often present. Arsenic is not an unusual contamination. Alcohol dissolves the dye and leaves sodium sulphate and carbonate insoluble. The dye may be precipitated by saturating the aqueous solution with purified common salt, while sodium carbonate and sulphate remain in solution. The sulphate of sodium contained in the residue left on ignition represents that formed from the sulphonate, as well as that pre-existing as sulphate. Pure sodium triphenylrosaniline-monosulphonate will yield 22.6% of Na_2SO_4 on fusion with sodium carbonate and nitre. On ignition alone a low result is obtained, the sodium present being insufficient to fix all the sulphur, besides which more or less sulphide and sulphite will probably be formed.

Sodium triphenylpararosaniline-monosulphonate is known in commerce as *Alkali Blue D.*[1] In its reactions it closely resembles its homologue from rosaniline, but is nearly insoluble in cold water, and in hot water forms a blue solution which has an odour of diphenylamine.

Triphenylrosaniline-disulphonic acid, having the formula $C_{20}H_{14}(SO_3H)_2(C_6H_5)_3N_3$, is obtained, together with the trisulphonic acid, when triphenylrosaniline hydrochloride (Spirit Blue) is digested

[1] Also known as *Methyl Alkali Blue* and *Alkali Blue 6 B*.

with 4 or 5 parts of strong sulphuric acid at 60° for 5 or 6 hours, and the temperature finally increased to 100°–110°. If the product be diluted with 3 or 4 times the quantity of water, both sulphonic acids are precipitated, but if a comparatively large quantity of water be used the precipitate consists mainly of the disulphonic acid, while the trisulphonic acid dissolves and may be obtained as a blue precipitate by treating the filtrate with common salt or hydrochloric acid in excess. Triphenylrosaniline-disulphonic acid is slightly soluble in water, but insoluble in acid liquids, and hence is thrown down as a blue precipitate on acidifying the solution of one of its salts. Excess of alkali turns the solution of its salts yellow. The sodium salt occurs in commerce under the name of *Silk Blue*, and *Bavarian Blue BSF*, *Methyl Blue for Silk MLB*, *Marine Blue B*, consists principally of the corresponding derivative of pararosaniline; while *Blackley Blue* is the sodium salt of diphenyl-tolylrosaniline-sulphonic acid.

Triphenylrosaniline-trisulphonic acid, of the composition $C_{20}H_{13}(SO_3Na)_3(C_6H_5)_3N_3$, is obtained as indicated above. It is soluble in water and alcohol. The *sodium*, *ammonium* and *calcium salts*, mixed with more or less of the corresponding disulphonates, form the commercial colouring matters known as *Water Blue*, *Cotton Blue*, etc. (page 252). The *ammonium* salt forms dark lumps or grains having a coppery lustre; the *sodium* salt usually occurs as dark blue irregular lumps. *China Blue* is a very porous variety of Water Blue, obtained by adding ammonium carbonate to a very concentrated and slightly acid solution of the colouring matter.

Water Blue is more soluble than Alkali Blue, and crystallises from its concentrated hot solution in flakes having a metallic lustre. Its solution is not completely precipitated by hydrochloric acid, under any circumstances; and not at all unless a large excess of the reagent be used or disulphonate be present. Sodium hydroxide decolourises the solution or turns it reddish-brown. Water Blue dissolves in strong sulphuric acid with dark yellowish-red colour, and on dilution a blue solution is formed, sometimes accompanied by partial precipitation.

Water Blue differs from Alkali Blue in not being taken up by wool from an alkaline solution, and hence the fibre so treated is not rendered blue by subsequent immersion in dilute acid.

Strong sulphuric acid dissolves Water Blue from fibres dyed with it, with a blue colouration, and a hydrochloric acid solution of stannous chloride behaves similarly. Sodium hydroxide turns the fibre reddish-

brown, and ammonia decolourises it immediately. Alcohol has no effect on the dyed fibre, even when boiling.

Water Blue is chiefly used for dyeing cotton, being fixed by means of tannin, or by alizarin oil, in conjunction with aluminium, antimony, or tin compounds. It is dyed on silk and wool in an acid bath, and in this case is always used in conjunction with other colouring matters.

The colouring matters known as *Bavarian Blue DBF*, *Methyl Blue M*, *BI for Cotton*, etc., chiefly consist of the sodium salt of *triphenyl-pararosaniline-trisulphonic acid*, and closely resemble the homologue, ordinary Water Blue.

Dyestuffs from tetramethyldiaminobenzophenone (Michler's ketone) and the corresponding hydrol.

In the general account of the general methods by which triphenylmethane dyestuffs can be obtained, mention has been made of the condensations which can be effected with the aid of Michler's ketone and the corresponding hydrol. With the aid of these substances the following dyestuffs among others have been prepared.

Victoria Blue B or **BS** is the hydrochloride of tetramethyl-phenyl-triamino-α-naphthyl-diphenylcarbinol, and is prepared by the action of phenyl-α-naphthylamine on tetramethyl-diamino-benzophenone chloride. It is sparingly soluble in cold, but readily so in hot water, yielding a blue solution which gradually deposits a reddish resinous precipitate of free base on boiling. This decomposition is prevented by the addition of acetic acid. In the presence of mineral acids the dyestuff is less soluble than in pure water. When dyed on wool Victoria Blue is very liable to rub; this fault may be avoided by boiling the wool with aluminium sulphate before dyeing.

Victoria Blue 4 R is obtained by the condensation of Michler's ketone with methyl-phenyl-α-naphthylamine and greatly resembles the preceding dyestuff in its general properties but dyes a redder shade.

Victoria Blue R is similarly obtained with ethyl-α-naphthylamine.

Night Blue is prepared from tetramethyldiaminobenzophenone and p-tolyl-α-naphthylamine. It is soluble in water with a fine blue colour which becomes turbid and is precipitated by boiling. Its solubility is increased by the addition of acetic acid. From the fact that Night Blue is completely precipitated from its solution by many other dyestuffs such as picric acid, Naphthol-Yellow, etc., it is used as a reagent for the quantitative estimation of such dyestuffs.

Chrome Blue, obtained by the condensation of tetramethyldiamino-

benzhydrol with hydroxynaphthoic acid, has been already referred to; the ortho-position of the carboxyl to the hydroxyl group makes it a mordant dyestuff, the lakes produced with chromium salts being green in colour.

Chrome Violet (Bayer) is a similar dyestuff in which salicylic acid is used as a component; it must not be confused with the *Chrome Violet* produced by J. R. Geigy of Basel.

Chrome Green is prepared with the aid of benzoic acid; it may be regarded as a carboxylic derivative of Malachite Green.

Alkylated Rosanilines.—The dyestuffs which occur as different marks of *methyl violet* (aniline violets) are prepared by the oxidation of dimethylaniline, by condensation of the chloride of Michler's ketone with dimethylaniline or from Michler's hydrol with subsequent oxidation.

The aniline violets are usually greenish powders or crystals with metallic reflection, soluble in water to fine violet solutions which dye silk and wool violet without a mordant. They can be fixed on cotton by tannin and tartar-emetic. The aniline violets are decolorised by boiling with potassium cyanide, a turbid solution being produced. With sulphuric acid they dissolve with yellow or brownish-yellow colour, and present a very close analytical resemblance, as will be seen in the annexed tables of their physical characters and chemical reactions.

Methyl Violet B, *Methyl-aniline Violet, Paris Violet, Dahlia, Direct Violet, Methyl Violet 2 B, or Methyl Violet V3* (page 280), is the hydrochloride or double zinc salt of pentamethyl-pararosaniline. It is produced by the direct oxidation of dimethylaniline (free from dimethyl-toluidine) by cupric chloride:

$$3C_6H_5.N(CH_3)_2 + 3O = 3H_2O + C_{19}H_{12}(CH_3)_5N_3.$$

A colouring matter known as *Chloranil-Violet*, probably identical with Methyl-violet, is obtained by the action of dimethylaniline on chloranil (tetrachloroquinone).

Methyl-aniline Violet occurs in commerce as a hydrochloride and also a compound of this salt with zinc chloride. The hydrochloride forms small crystals, the zinc double salt a powder or irregular lumps. Both varieties of the colouring matter exhibit a green metallic reflection and are easily soluble in water, alcohol, amyl alcohol, and chloroform.

Dilute solutions of Methyl-Violet are turned pure blue by a very

small addition of hydrochloric acid. With more acid they appear green in thin layers, but red and somewhat turbid in thicker strata. Excess of acid turns the solution red or yellowish-brown from the formation of an acid salt. Ammonia produces a lilac and sodium hydroxide a violet-brown precipitate, the solution becoming colourless on boiling.

With chromic acid Methyl-Violet gives a dirty violet and with stannous chloride a blue-violet precipitate, becoming lighter on boiling. Hypochlorites decolourise solutions of Methyl Violet.

Methyl-Violet is completely precipitated by soluble ferrocyanides and ferricyanides, and hence may be conveniently fixed on cotton mordanted with potassium ferrocyanide, or in the fibres on which zinc ferrocyanide has been previously deposited by double decomposition. In this manner methyl-violet may be used for printing calico. It is also fixed by albumin or tannin, and is used for topping goods dyed with iron mordants and alizarin, in order to brighten the fast violet thus produced.

Boiling with water gradually decolourises fibres dyed with Methyl Violet. Hydrochloric acid removes part of the colour and the fibre becomes greenish-yellow, but the original colour is restored on washing with water. Ammonia decolourises the fibre. Sodium hydroxide turns it Reddish-Violet and gradually decolourises it. Treated with a hydrochloric acid solution of stannous chloride, the fibre becomes a yellow or greenish-yellow colour.

Methyl-Violet is liable to much the same adulterations as other aniline dyes. It may be estimated volumetrically by precipitation with picric acid, the formula of the picrate being $C_{24}H_{27}N_3.C_6H_2(NO_2)_3OH$.

Crystal Violet, *Violet C*, *Crystal Violet 5 BO*, or *Crystal Violet O* is the hydrochloride of hexamethyl-pararosaniline. It is obtained by action of tetra-methyl-diamino-benzophenone chloride or carbon oxychloride on dimethyl-aniline.

Crystal Violet forms long hexagonal prisms or pyramids. The crystals have a beetle-green reflection if anhydrous, but a variety containing $8H_2O$ also occurs, the reflection from which is bronze. When heated at 100°, the crystals become brown and suffer slight decomposition. Crystal Violet is soluble both in water and alcohol, but crystallises more readily from the former than the latter menstruum. The solutions are deep violet-blue, and dye wool and silk a very blue shade

of violet. On cotton, Crystal Violet is fixed by tannin and tartar-emetic.

On heating Crystal Violet in a closed tube to 120° with an aqueous solution of ammonium sulphide, a leuco-base is formed of the formula $C_{25}H_{21}N_3$, which melts at 173° after being purified by crystallisation from alcohol.

Crystal Violet forms a very insoluble picrate, a fact which may be utilised for its estimation and assay.

Benzyl Violet is prepared by the action of benzyl chloride on Methyl Violet in presence of an alkali and occurs commercially as the hydrochloride or zinc double salt. It dyes a bluer shade than Methyl Violet (it is sometimes put on the market as *Methyl-Violet 6B* or 7 *B*); the fibre dyed with it is turned light blue by sodium hydroxide, whereas it turns red-violet if dyed with Methyl-Violet. In both cases the material is eventually decolourised.

Acid Violets.—There are several of these dyestuffs, which in general resemble Acid Magenta, but give a bluer shade in dyeing. For the most part they are sodium salts of the sulphonic acids of methyl- and ethyl-rosaniline and pararosaline. The shades are usually quite fast to light and resist milling fairly well, but are destroyed by alkalies. Among these violets are to be found *Red Violet* 4 RS,[1] and 5 RS, which are the sodium trisulphonates of dimethylrosaniline and ethylrosaniline respectively; *Acid Violet* 6 B[2] or *Acid Violet* 4 BN is the sodium sulphonate of benzyl-pentamethyl-pararosaniline.

Formyl Violet S 4 B[3] is also a rosaniline violet which is obtained by the condensation of diethyldibenzyldiamino-diphenyl-methane-disulphonic acid with diethylaniline. It gives a bluer shade than Acid Magenta and resembles the acid violets very closely.

Acid violets of a red shade which have been made by the alkylation of Acid Magenta, usually contain some excess of the latter. In order to effect a separation of the magenta from the Acid Violet the colouring matter is dissolved in hot water and precipitated with basic lead acetate. The precipitate is decomposed by ammonium carbonate, and filtered; the colouring matter in the filtrate being estimated by evaporation and weighing the residue. The washings are acidified with sul-

[1] Also called Acid Violet 4 RS.

[2] There is also an Acid Violet 6 B made by the Berlin Aniline Works which is the sodium sulphonate of dimethyl-dibenzyl-diethyl-triaminotriphenyl carbinol. Acid violet 4 BN is also known as Acid Violet 7 B and Acid Violet N. Wool Blue S is a mixture of acid violet 4 BN with a light green.

[3] Also known as Acid Violet 4 B extra, Acid Violet 6 B (of Geigy).

phuric acid, then made alkaline with lime, and filtered. The filtrate is evaporated to dryness and treated with alcohol, which extracts the calcium salts of the violet colouring matters, leaving that of the acid magenta undissolved. The shade of the precipitate and the 2 portions of the washings can be ascertained by dye trials.

Aniline Greens.—The effect of amino- and alkylated amino-groups in altering the shade of a compound is generally very pronounced and reapeated attention has been called to this phenomenon not merely in the triphenylmethane series, but among other groups of dyestuffs as well. But if a dialkylamino-group be converted into a trialkylammonium salt group by the addition of a molecule of alkyl-halide or other ester, the auxochromic effect is generally inhibited.

An excellent example of this behaviour is shown by Malachite Green and Crystal Violet and the substances obtained by the alkylation of the latter dyestuff. Crystal Violet differs from malachite green by the possession of an extra *p*-dimethylamino-group in the third benzene nucleus. If, however, this third dimethylamino-group be converted by the action of methyl chloride into a trimethyl-ammonium chloride group, Methyl Green is obtained. The relationship is rendered clear by consideration of the formulæ:

$$C\begin{cases}.C_6H_5\\ .C_6H_4.N(CH_3)_2\\ :C_6H_4:N(CH_3)_2Cl\end{cases} \qquad C\begin{cases}.C_6H_4.N(CH_3)_2\\ .C_6H_4.N(CH_3)_2.\\ :C_6H_4:N(CH_3)_2Cl\end{cases} \qquad C\begin{cases}.C_6H_4.N(CH_3)_3Cl\\ .C_6H_4.N(CH_3)_2\\ :C_6H_4:N(CH_3)_2Cl\end{cases}$$

Malachite Green. Crystal Violet. Methyl Green.

The dyestuffs of this class are now used less frequently than formerly, they suffer from the disadvantage that on warming, alkyl halide is removed and Methyl-Violet results.

Iodine Green (*Night Green* or *Pomona Green*) was formerly prepared by alkylation with methyl iodide; such a dyestuff will give off violet iodine vapours on heating with concentrated sulphuric acid.

Methyl Green (*Methylaniline Green, Paris Green, Light Green, Double Green*, or *Green Powder*) is prepared by the action of a slow stream of methyl chloride on an alcoholic solution of Methyl Violet heated to 40°, the solution being kept neutral by successive additions of sodium hydroxide; autoclaves are not necessary for this purpose. The alcohol is subsequently distilled off, water added, any Methyl-Violet still present

removed by sodium carbonate and salt and the Methyl Green precipitated by zinc chloride as the double salt.

The corresponding *Ethyl Green* obtained by the action of ethyl bromide on Methyl Violet was also prepared in the action of a zinc double salt, possibly of the formula $C_{25}H_{30}N_3Cl,C_2H_5Br, ZnCl_2$. Ethyl Green dyes a yellower shade than Methyl Green but both dyes have been practically displaced by the green dyestuffs of the malachite green series which are not only of greater dyeing power but also cheaper to manufacture.

Rosolic Acid and Aurin Group.—The compounds of this series are analogues of rosaniline and pararosaniline, the amino- and imonium salt groups of the latter compounds being replaced by hydroxyl and oxygen respectively.

$$C\left\{\begin{array}{l}.C_6H_4.NH_2\\ .C_6H_4.NH_2\\ :C_6H_4:NH_2Cl\end{array}\right. \qquad\qquad C\left\{\begin{array}{l}.C_6H_4.OH\\ .C_6H_4.OH\\ :C_6H_4:O\end{array}\right.$$

Pararosaniline. Aurin.

The name "*Rosolic acid*" (Rosolsäure) was given by Runge to a product which he obtained by the oxidation of crude phenol, while Kolbe and Schmidt gave the name of "*Aurin*" to a dyestuff which they obtained by heating phenol and oxalic acid with concentrated sulphuric acid

$$C_2O_4H_2 + 3\,C_6H_5OH = CO + 3\,H_2O + C_{19}H_{14}O_3$$

The 2 compounds are evidently closely related; considerable confusion was experienced until E. and O. Fischer pointed out that the substances were homologous, aurin being obtained from pararosaniline by the diazo-reaction in the same way that Caro and Wanklyn had in 1865 obtained rosolic acid from rosaniline.

Both substances are phenolic in character, they may be reduced to leuco-compounds (trihydroxytriphenylmethane and its next higher homologue), and, moreover, show weak basic properties giving salts with acids which are readily hydrolysed. To the latter compounds either an oxonium or carbonium structure may be assigned.

$$C\begin{cases} .C_6H_4.OH \\ .C_6H_4.OH \\ :C_6H_4:O\begin{cases} H \\ Cl \end{cases} \end{cases} \quad \text{or} \quad C\begin{cases} .C_6H_4.OH \\ .C_6H_4.OH \\ :C_6H_4:\begin{cases} OH \\ Cl \end{cases} \end{cases}$$

When heated with ammonia, partial or total replacement of hydroxyl and ketonic oxygen by amino- and imino-groups may result; in the former case *Coralline* or *Peonine* is produced, in the latter rosaniline or pararosaniline according to whether rosolic acid or aurin has been employed for the reaction.

Pure aurin may be obtained from the commercial product by passing ammonia gas through a saturated alcoholic solution of the latter, when steel-blue crystals of ammonium aurate, $C_{19}H_{12}O.(ONH_4)_2$, are deposited, the impurities remaining in solution. The washed precipitate may be decomposed by dilute hydrochloric or acetic acid, or simply exposed to the air, when ammonia volatilizes and pure aurin remains.

When pure, aurin forms crystalline needles having an adamantine lustre and the colour of chromic acid, or else of a darker shade with a blue or greenish-blue reflection. Aurin is fusible, but not volatile without decomposition.

Commercial Aurin or rosolic acid contains a molecule or two of water, and is a dark amorphous substance with a beetle-green lustre. The powder is red.

Aurin and rosaurin (rosolic acid) are but slightly soluble in water, though their solutions have a reddish-yellow colour. They dissolve very readily in hot alcohol, somewhat sparingly in cold, and are also moderately soluble in glacial acetic acid, phenol, creosote, and in ether, but are insoluble in benzene and carbon disulphade.

Aurin and rosaurin dissolve readily in solutions of ammonia and fixed alkalies to form solutions which are bluish-red when dilute and yellowish-red when concentrated. A characteristic change in the absorption-spectrum occurs on dilution.

Aurin and rosaurin have the property of combining both with acids and bases. The former compounds are the more definite; but ether extracts aurin and rosaurin from its acidified solutions and not from its alkaline solutions.

Solutions of aurin are decolourised when heated with sodium amalgam, or sodium hydroxide and zinc-dust, colourless hydraurin, $C_{19}H_{16}O_3$, being formed. The alkaline solution is also decolourised

by heating with excess of potassium cyanide, and on cooling and acidifying white crystalline flocks of hydrocyanaurin, $C_{20}H_{15}NO_3$, are thrown down.

Yellow Coralline.—This colouring matter is prepared by treating 8 parts of pure phenol in the cold with 3.2 parts of strong sulphuric acid, and after some hours adding 4.8 parts of oxalic acid, and heating the whole to 110° for 24 hours. In addition to aurin and methyl-aurin, more or less oxidised aurin, and pseudo-rosolic acid or coralline-phthaleïn, $C_{20}H_{16}O_4$, are also produced, and a sublimate of phenyl oxalate has been observed to be formed. The melt is poured into water and purified by treatment with boiling water. The product is Yellow Coralline, and forms a brown resinous substance having a green metallic lustre. It contains about 20% of aurin, besides crystalline derivatives of rosolic acid, and resinous bodies. Its reactions are identical with those of aurin. The soluble sodium salt of Red Coralline is also called "yellow coralline."

Red Coralline or Peonine is prepared by heating 2 parts of Yellow Coralline with 1 of strong ammonia to 120°–140°, when one of the hydroxyl groups is replaced with formation of the substance, $C_{19}H_{13}O_2(NH_2)$, which is precipitated on pouring the liquid into water and acidifying. The product is "Spirit Soluble" Red Coralline, "water soluble" coralline being the ammonium salt. The first forms lumps with a metallic lustre; the latter a brownish-red porous mass, soluble in concentrated sulphuric acid with yellow colour. The red aqueous solution of the ammonium salt is unaltered by alkalies and precipitated yellow by acids. Basic lead acetate and aluminium acetate produce orange or yellow precipitates.

Eupittonic acid has the constitution of a hexa-methyl-aurin, but as a dyestuff it is now obsolete.

Chrome Violet (Geigy).—Aurin-tricarboxylic acid and its homologues may be obtained by the condensation of formaldehyde with salicylic acid in sulphuric acid solution and simultaneous oxidation. The process was discovered by Sandmeyer (German patent 49,970); generally nitrous acid is used as the oxidising agent and since methyl alcohol is oxidised to formaldehyde by nitrous acid the colouring matter may be produced by heating together a mixture of methyl alcohol, sulphuric acid, salicylic acid and sodium nitrite. The action evidently takes place in two stages, a diphenylmethane derivative being first

formed which undergoes subsequent condensation with salicylic acid under the influence of the oxidising agent.

$$CH_2O + 2C_6H_4(OH)(COOH) = H_2O + CH_2\left((1)C_6H_3\begin{cases}(4)OH\\(3)COOH\end{cases}\right)_2$$

$$CH_2\left(C_6H_3\begin{cases}OH\\COOH\end{cases}\right)_2 + C_6H_4\begin{cases}OH\\COOH\end{cases} + 2O =$$

$$2H_2O + C\begin{cases}.C_6H_3(OH)(COOH)\\.C_6H_3(OH)(COOH)\\:C_6H_3\begin{cases}:O\\.COOH\end{cases}\end{cases}$$

The colouring matter gives reddish-violet shades on chromium mordants; these are very fast to soap.

Mixed dyestuffs are easily obtained if the 2 stages of the action are carried out separately; the formaldehyde is first condensed with one phenol or hydroxycarboxylic acid and the resulting diphenylmethane derivative condensed with another phenolic compound.

Phenolphthalein.—Phthalic acid condenses readily with phenols, amines and aminophenols forming compounds which may be classed among the derivatives of triphenylmethane. Should phenol itself be employed, a product, phenolphthaleïn, is obtained which certainly in its alkaline salts must be looked upon as a mono-hydroxyfuchsone-orthocarboxylic acid.[1] But on acidifying the purple solution of an alkaline salt a colourless compound containing 2 hydroxyl and no carboxyl groups is precipitated; this free phenolphthaleïn is regarded as a dihydroxydiphenylphthalide. The relationship of phenolphthaleïn to its quinonoid alkaline salts is apparent from the formulæ:

$$C_6H_4\begin{cases}.(1)\ C:(C_6H_4.OH)_2\\ \qquad\qquad >O\\.(2)CO\end{cases} \qquad C_6H_4\begin{cases}.C\begin{cases}:C_6H_4:O\\.C_6H_4.OH\end{cases}\\.COONa.\end{cases}$$

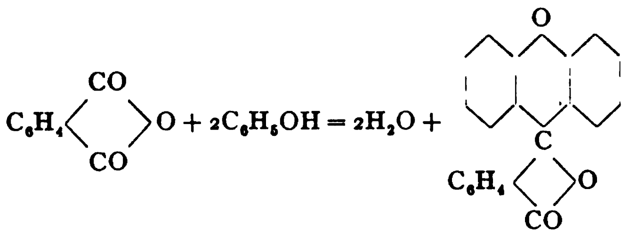
[1] The quinonoid constitution of phenolphthaleïn in alkaline solution is no longer based on the condensation with hydroxylamine observed by Friedländer (*Ber.*, 1893, **26**, 172, 2258) the supposed oxim probably possessing a different constitution to that first assigned to it. A far more satisfactory basis is the isolation by A. G. Green and P. E. King (*Ber.*, 1906, **39**, 2365; 1907, **40**, 3724; *Proc. Chem. Soc.*, 1907, **23**, 228; *J. Soc. Chem. Ind.*, 1908, **27**, 3; 1909, **28**, 63) of red quinonoid carboxylic esters

$$C_6H_4(CO_2Me).C\begin{cases}:C_6H_4:O\\.C_6H_4.OH\end{cases} \quad \text{and} \quad C_6H_4(CO_2Me).C\begin{cases}:C_6H_4:O\\.C_6H_4.OMe\end{cases}$$

which are isomeric respectively with the lactonoid ethers

$$\underbrace{C_6H_4.CO.O.C}\begin{cases}.C_6H_4.OMe\\.C_6H_4.OH\end{cases} \quad \text{and} \quad \underbrace{C_6H_4.CO.O.C}\begin{cases}.C_6H_4.OMe\\.C_6H_4.OMe\end{cases}$$ (See Vol. 3.)

In the case of phenol the condensation occurs chiefly in the para-position to the hydroxyl group, a small quantity undergoes ortho-condensation and elimination of water taking place, "*phenolphthalein-anhydride*" or *fluoran* is produced:



With dihydric phenols and amino-phenols condensation occurs normally with formation of hydroxy- and amino-fluorans (*e. g.*, fluorescein, rhodamine, etc.); since all these dyestuffs contain the pyrone ring it will be preferable to treat them with other dyestuffs containing the same nucleus and not consider them with other derivatives or triphenylmethane.

Phenolphthaleïn is dealt with in Vol. 3 (page 548).

Phenolphthaleïn while useless as a dyestuff is a valuable indicator. On account of its small dissociation constant ($K = 8 \times 10^{-10}$, Salm, *Zeit. Elektrochem*, 1906, **12**, 99) the colour of its alkaline solutions is discharged when the concentration of hydrogen ions is small; it is therefore a valuable indicator for weak acids, giving the point of neutralisation very sharply. As it reacts in alcoholic and ethereo-alcoholic solution it allows of the titration not merely of the soluble but also of many of the insoluble organic acids, including palmitic, stearic, oleic, linoleic, ricinoleic, the acids of colophony (pinic, pimaric, sylvic), etc. The alkaloids have generally no marked alkaline reaction on phenolphthaleïn, and hence the amount of acid in salts of morphine, quinine, cinchonine, quinidine, brucine, aniline, and urea, operating, if necessary, in alcoholic solution, can be ascertained by titration with standard alkali, just as if no organic base were present.

The value of phenolphthaleïn as an indicator of neutrality is completely vitiated by the presence of ammonium salts.

Phenolphthaleïn is readily soluble in alcohol. A 1% solution keeps perfectly, and a few drops are sufficient for each titration.

In using phenolphthaleïn as an indicator it must be kept in mind

that the only suitable standard alkaline solutions are sodium and potassium hydroxides; further that on heating with an excess of either of these reagents it is liable to decolourisation. An explanation of this phenomenon will be found in a paper by Green and Perkin (*Trans. Chem. Soc.*, 1904, **85**, 398).

General Analytic Properties of the Triphenylmethane Dyes.

The detection of dyestuffs on the fibre is treated in a separate section, but in identifying a given colouring matter by special tests the use of the following reagents should be kept in mind, concentrated and dilute sulphuric and hydrochloric acids, the dilute acids in both cases being of 10% strength, nitric acid (sp. gr. 1.40), ammonia (sp. gr. 0.91), sodium hydroxide (10% solution) and frequently a hydrochloric acid solution of stannous chloride.

The effect of concentrated sulphuric acid is to combine with the auxochromic amino-groups and inhibit their action so that Malachite Green, Magenta and Crystal Violet despite their differences in shade all give yellow or orange solutions in concentrated sulphuric acid. Concentrated hydrochloric acid produces much the same effect.

10% sulphuric acid will partially combine with auxochromic amino-groups and the same remark holds for hydrochloric acid of moderate dilution. The different marks of Methyl Violet and Crystal Violet give generally green or greenish-blue colourations with 10% sulphuric acid; Malachite Green goes to a darker shade under the same conditions while magenta if dissolved in concentrated sulphuric acid and then diluted gives a colourless solution. Generally, however, dilution of a strong sulphuric acid solution of a basic dyestuff eventually restores the original colour when sufficient water has keen added to hydrolyse the di- and tri-acid salts which may have been formed.

The action of nitric acid probably gives nitro-derivatives either of the original dyestuff or of its degradation products, the fact that many dyestuffs which give other shades with sulphuric and hydrochloric acid give yellow (brown, etc.) solutions with nitric acid points to a breaking up of the molecule.

Ammonia and sodium hydroxide often produce pale to nearly colourless precipitates in the case of basic dyestuffs of the triphenylmethane series, the solution being decolourised; this behaviour is of course explained by the production of colourless carbinol bases. The pre-

cipitates of the latter if collected and dissolved in dilute acids do not always immediately give solutions of the same shade as the original dyestuffs. This is well seen in the case of Malachite Green. Addition of alkali produces at first a yellow colour base which passes over gradually into tetramethyldiaminotriphenylcarbinol. The latter forms a colourless or greyish powder; it may be obtained by crystallisation from petroleum spirit as colourless leaflets or crystal aggregates of m. p. 120°. This colourless base dissolves to a nearly colourless solution in dilute acetic acid, the formation of colouring matter taking place by standing some time in the cold or more rapidly on heating. This behaviour is easily explained, a colourless acetate of the carbinol base is first formed which slowly loses water giving the acetate of malachite green.

$$C\left\{\begin{array}{l}.C_6H_5\\ .C_6H_4.N(CH_3)_2\\ .C_6H_4.N(CH_3)_2\\ .OH\end{array}\right. \rightarrow C\left\{\begin{array}{l}.C_6H_5\\ .C_6H_4.N(CH_3)_2\\ .C_6H_4.N(CH_3)_2,H.C_2H_3O_2\\ .OH\end{array}\right. \rightarrow$$

$$C\left\{\begin{array}{l}.C_6H_5\\ .C_6H_4.N(CH_3)_2\\ .C_6H_4:N(CH_3)_2.C_2H_3O_2\end{array}\right.$$

Stannous chloride in acid solution generally effects a more or less complete reduction to the corresponding leuco-compound, frequently the solutions are completely[1] decolourised, in other cases a difference of shade is observed. The greater or less ease with which the colouring matter is regenerated from the leuco-compound is frequently useful in giving an idea as to the class of compounds to which a given dyestuff belongs. (The process of subsequent reoxidation is of course inapplicable for azo-compounds since fission at the azo-linkages takes place, but with dyestuffs the molecules of which are not ruptured on reduction, is frequently of great use.)

A. G. Green has utilised this difference in rate of oxidation of the leuco-compounds in his scheme for the qualitative analysis of artificial dyestuffs (*J. Chem. Soc. Ind.*, 1893, **12**, 3), and points out that there are 2 classes into which the colouring matters may be divided.

[1] In the case of the triphenylmethane dyes the action with stannous chloride is slow, the different marks of methyl violet acquire a bluish or greenish shade while magenta and New Fuchsine are only slowly decolourised. Many dystuffs on the other hand with rings of such type as thiazine, acridine, etc., are rapidly decolourised.

1. Colours whose leuco-compounds are not readily reoxidised on exposure to the air; in this class are included all colouring matters of the triphenylmethane series, the phthaleïns or pyrone colours, indophenols and indamines.

2. Colours whose leuco-compounds are rapidly reoxidised on exposure to air; these colours belong to one of the following classes, azines, oxazines, thiazines, quinoline and acridine colours, hydroxyanthraquinone colours, thiazole colours and indigo.

In explanation of this difference in behaviour Green has suggested that the colours of Class 1 are of para-quinonoid, those of Class 2 of ortho-quinonoid type (*Proc. Chem. Soc.*, 1892, **8**, 195; 1896, **12**, 226).

The reviser of this and the succeeding sections (to sulphur dyes included) desires to acknowledge the help obtained by reference to the works of Cain and Thorpe, Friedländer, Herrmann, Nietzki, Schultz and Julius (translation by Green), and further to tender his thanks to Messrs. Cassella & Co. of Frankfort, the Chemische Fabrik Griesheim-Elektron, Messrs. Kalle & Co., of Biebrich and the Society of Chemical Industry in Basle for the information they have so kindly placed at his disposal.

Commercial name	Formula	Remarks
Acid Magenta, Fuchsine S. Rubine S.	$C\begin{cases}(1)C_6H_3\begin{cases}(3)SO_3Na\\(4)NH_2\end{cases}\\=(1)C_6H_3\begin{cases}(3).SO_2\\(4)NH_2\end{cases}>O\\(1)C_6H_3\begin{cases}(3)SO_3Na\\(4)NH_2\end{cases}\end{cases}$	Sulphonation of fuchsine.
Acid Violet 6B. Guinea Violet 4B.	$C\begin{cases}(1)C_6H_4(4)N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_3Na\end{cases}\\=(1)C_6H_4(4)=N(CH_3)_2—O\\(1)C_6H_4(4)N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_2\end{cases}\end{cases}$	....
Acid Violet 7B.	$C\begin{cases}(1)C_6H_4\ (4)\ N\begin{cases}CH_3\\C_6H_4.SO_3Na\end{cases}\\=(1)C_6H_4(4)=N(C_2H_5)_2—\\(1)C_6H_4\ (4)\ N\begin{cases}CH_3\\C_6H_4.SO_2.O\end{cases}\end{cases}$	....
Acid Violet 5BK (Kalle).	....	....
Acid Violet 4BN, 6B, 7BN.	$C(OH)\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_4(4)N\begin{cases}CH_3\\CH_2.C_6H_4.SO_3Na\end{cases}\end{cases}$	....
Acid Violet 6BN.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\=(1)C_6H_2\begin{cases}(1)OC_2H_5\\(4):NH(C_6H_4CH_3)—\\(5)—SO_2——O\end{cases}\\(1)C_6H_4(4)N(CH_3)_2\end{cases}$	....
Acid Violet 7BN.	$C\begin{cases}(1)C_6H_4(4).N\begin{cases}CH_3\\C_6H_4.SO_2\end{cases}\\=(1)C_6H_4(4):N\ (CH_3)\ _2.O\\(1)C_6H_4(4).N\begin{cases}CH_3\\C_6H_4.SO_3Na\end{cases}\end{cases}$	From dimethyl-amino-benzoic acid and 2 molecules methyl-diphenyl amine-sulphonic acid.
Acid Violet 7 BS, 5 BNS, 6 BNS.	....	From alkylated β-naphthyl-amine.
Acid Violet 6BW.	$C(OH)\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_2\begin{cases}(2)OC_2H_5\\(4)NH.C_6H_4.CH_3\\(5)SO_3Na\end{cases}\end{cases}$	....

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Green crystals red solution.	Decolourised.	No change.	Yellow.	Red.	Acid dyestuff. Slightly soluble in alcohol. But slightly affected with stannous chloride in hydrochloric acid.
Violet powder, violet solution.	Light blue.	Bluish-green.	Brown.	Bluish-green.	Acid dyestuff.
Violet powder, violet solution.	Violet precipitate.	Green.	Orange.	Violet.	Acid dyestuff.
Violet powder.	Lighter.	....	Orange.	....	Dyes wool violet: on the fibre gives following reactions: Hydrochloric acid; green sodium hydroxide, slightly decolourised; conc. sulphuric acid, orange solution.
Violet powder, violet solution.	Blue ppt. Colourless solution on warming.	Blue ppt.	Yellow.	Blue.	Colours wood a bluish-violet.
Violet powder, violet-blue solution.	Slowly decolourised.	Red-brown with excess of acid.	Orange solution.	Violet-red then blue-violet.	Dyes silk and wool from an acid bath.
Blue-violet powder, blue solution.	Decolourised on warming.	Green.	Orange.	Blue.	Dyes wool and silk bluish-violet from an acid bath.
Violet solution in water or alcohol.	Blue if cold, lighter when heated.	Violet ppt. With more acid, green, then yellowish-brown.	Yellowish-brown.	Green then blue.	
Violet powder, violet solution.	Decolourised.	Redder.	Orange.	Violet.	Acid dye.

Commercial name	Formula	Remarks
Alkali Blue, Nicholson's Blue, Fast Blue	$C(OH) \begin{cases} (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NH.C_6H_5 \end{cases} \\ (1)C_6H_4(4)NH.C_6H_5 \\ (1)C_6H_4(4).NH.C_6H_4.SO_3Na \end{cases}$	Sulphonation of triphenyl-rosaniline.
Alkali Blue D and 6B, Methyl Alkali Blue, etc.	$C(OH) \begin{cases} (1)C_6H_4(4)NH.C_6H_5 \\ (1)C_6H_4(4)NH.C_6H_5 \\ (1)C_6H_4(4)NH.C_6H_4.SO_3Na \end{cases}$	Sulphonation of diphenylamine blue.
Alkali Blue XG, Soluble Blue XG.	....	....
Alkali Green, Viridine.	$C \begin{cases} (1)C_6H_5 \\ (1)C_6H_4(4)NH.C_6H_5 \\ (1)C_6H_4(4)=NH.C_6H_4.SO_2 \\ \quad\quad\quad\quad\;\; \lfloor\_\_\_\_\_\_ O \rfloor \end{cases}$	....
Alkali Violet 6B.	$C \begin{cases} (1)C_6H_4(4)N(C_2H_5)_2 \\ =(1)C_6H_4(4):N(C_2H_5)_2 — \\ (1)C_6H_4(4)N \begin{cases} C_6H_4.SO_2.O \\ CH_3 \end{cases} \end{cases}$	Condensation of tetraethyl-diamino-benzophenone with methyl-diphenylamine and sulphonation.
Alpine Blue.	....	....
Aurin. Pararosolic acid.	$C \begin{cases} (1)C_6H_4(4)OH \\ (1)C_6H_4(4)OH \\ (1)C_6H_4(4):O \end{cases}$	From phenol and oxalic acid condensed with concentrated sulphuric acid.
Aurotine.	$C \begin{cases} (1)C_6H_2 \begin{cases} (3)NO_2 \\ (4)ONa \\ (5)NO_2 \end{cases} \\ (1)C_6H_2 \begin{cases} (3)NO_2 \\ (4)ONa \\ (5)NO_2 \end{cases} \\ C_6H_4.CO.O \end{cases}$	By nitration of phenolphthalein.
Azo-Green.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ =(1)C_6H_4(4)=N(CH_3)_2 — O \\ (1)C_6H_4(3).N:N(1)C_6H_4 \begin{cases} (3)CO \\ (4)OH \end{cases} \end{cases}$	....
Azuline.	....	....

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Dark blue powder, blue solution.	Brown.	Blue ppt.	Red.	Blue ppt.	Acid dye. Nitric acid (sp. gr. 1.40); green with dark edge.
Dark blue powder, blue solution.	Brown.	Blue ppt.	Brown.	Blue ppt.	Acid dye.
Black lumps, greenish-blue solution.	Black ppt.	Blue ppt.	Brown.	Blue ppt.	Acid dye.
Green powder, green solution.	Brown.	Green ppt.	Red.	Green ppt.	Obsolete.
Violet powder, bluish-violet solution.	Blue ppt. Colourless on warming.	First a blue ppt. then orange solution with more acid.	Yellowish-brown solution.	First olive-green then blue.	Dyes wool blue-violet from alkaline, neutral or acid bath.
Brown lumps insoluble in water.	Dissolves in sodium hydroxide with cherry-red colour.	Insoluble.	Yellow solution.	Reprecipitated.	Soluble in alcohol.
Yellow powder, yellow solution.	No change.	Precipitate.	....	....	Acid or mordant dye for wood.
Green paste, green solution.	Clear solution.	Red.	Brown.	Red ppt.	Mordant dyestuff, used on chromed wool.
A name applied to impure diphenylamine blue.	....	....	Yellow.	Blue ppt.	Dark blue powder, soluble in alcohol, insoluble in water. (Obsolete.)

Commercial name	Formula	Remarks
Bavarian Blue DSF. Methyl blue water soluble. Navy Blue B. Methyl Blue for silk MLB.	$C\begin{cases}(1)C_6H_4(4)NH.C_6H_4.SO_3Na\\ =(1)C_6H_4(4):NH(C_6H_4)\text{—}\\ (1)C_6H_4(4).NH.C_6H_4.SO_2.O\end{cases}$	Sulphonation of diphenylamine blue.
Benzyl violet. Paris violet 6B. Methyl violet 6B, 7B. Violet 5B. Violet 6B.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ =(1)C_6H_4(4)=N(CH_3)_2Cl\\ (1)C_6H_4(4)N\begin{cases}CH_3\\ CH_2.C_6H_5\end{cases}\end{cases}$	....
Biebrich Acid Blue (Kalle).	....	....
Bradford Blue.	....	....
Chrome Blue.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ =(1)C_6H_4(4):N(CH_3)_2\text{—}\\ (4)C_{10}H_5\begin{cases}(2).CO\text{—}O\\ (2).OH\end{cases}\end{cases}$	....
Chrome Green.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ =(1)C_6H_4(4):N(CH_3)_2\text{—}\\ (1)C_6H_4(3).CO\text{—}O\end{cases}$	....
Chrome Violet (Bayer).	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ =(1)C_6H_4(4)N(CH_3)_2\text{—}\\ (1)C_6H_3\begin{cases}(3).CO\text{—}O\\ (4)OH\end{cases}\end{cases}$	By condensation of Michler's hydrol with salicylic acid and subsequent oxidation.
Chrome Violet (Geigy).	$C\begin{cases}(1)C_6H_3\begin{cases}(3)COONa\\ (4)OH\end{cases}\\ =(1)C_6H_3\begin{cases}(3)COONa\\ (4):O\end{cases}\\ (1)C_6H_3\begin{cases}(3)COONa\\ (4)OH\end{cases}\end{cases}$	By condensation of formaldehyde with salicylic acid in presence of an oxidising agent.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Indigo blue powder, blue solution.	Red.	Darker.	Brown.	Blue.	Blue dye for silk.
Metallic powder, violet solution.	Brown ppt. and colour.	Brown.	Yellow.	Violet.	Basic dye. Soluble in alcohol.
Dark blue powder.	....	....	Yellow.	....	Dyes wool a greenish-blue. Gives following reactions on fibre: Hydrochloric acid, greenish-yellow; sodium hydroxide, slightly decolourised; concentrated sulphuric acid, yellow solution.
Bronzy powder, violet solution.	Brown ppt.	Blue ppt.	Brown ppt.	Blue ppt.	Soluble in alcohol. (Obsolete.)
Black paste, blue solution.	No change.	Brown.	Red.	Brown.	Soluble in alcohol. Mordant dye for wool.
Brown powder, Green solution.	Decolourised.	Orange.	Orange.	No change.	Soluble in alcohol.
Black paste, insoluble.	Violet solution and black precipitate.	Brown.	Brown.	Redder.	Soluble in alcohol. Mordant dye.
Brown powder, red solution.	Brown.	Precipitate.	Brown.	Precipitate.	For calico printing.

Commercial name	Formula	Remarks
Coralline Aurin R. Red Coralline Peonine.	$C \begin{cases} (1)C_6H_4(4)OH \\ =(1)C_6H_4(4):O \\ (1)C_6H_4(4)NH_2 \end{cases}$	By action of ammonia on aurin.
Crystal Violet. Crystal Violet 5B-O, O. Violet C. Violet 7B extra.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ =(1)C_6H_4(4):N(CH_3)_2Cl \\ (1)C_6H_4(4)N(CH_3)_2 \end{cases}$	....
Cyanine B.	....	By oxidation of patent blue V.
Cyanol Extra. Acid Blue 6 G.	$C \begin{cases} (1)C_6H_3 \begin{cases} (3)CH_3 \\ (4)NHC_2H_5 \end{cases} \\ =(1)C_6H_3 \begin{cases} (3)CH_3 \\ (4):NH(C_2H_5)— \end{cases} \\ (1)C_6H_2 \begin{cases} (2).SO_2—O \\ (4)SO_3Na \\ (5)OH \end{cases} \end{cases}$	....
Diphenylamine Blue spirit soluble Bavarian Blue spirit soluble XL Opal Blue.	$C \begin{cases} (1)C_6H_4(4)NH.C_6H_5 \\ =(1)C_6H_4(4):NH(C_6H_5)Cl \\ (1)C_6H_4(4)NH.C_6H_5 \end{cases}$	Action of aniline on *p*-rosaniline.
Eriocyanine A.	$C \begin{cases} C_6H_3 \begin{cases} N(CH_3)_2 \\ SO_3Na \end{cases} \\ =C_6H_4=N(CH_3)_2— \\ (1)C_6H_3 \begin{cases} (2)SO_2.O— \\ (4)N(CH_2.C_6H_5)_2 \end{cases} \end{cases}$	....
Erioglaucine A.	$C \begin{cases} (1)C_6H_4(4)N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{cases} \\ =(1)C_6H_4(4):N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{cases} \\ (1)C_6H_4(2).SO_2.O \end{cases}$	By condensation of benzaldehyde *o*-sulphonic acid with ethyl-benzyl-aniline and subsequent oxidation.
EthylGreen Malachite Green G. New VictoriaGreen Emerald Green. Fast Green S.	$C \begin{cases} C_6H_5 \\ =(1)C_6H_4(4):N(C_2H_5)_2SO_4H \\ (1)C_6H_4(4)N(C_2H_5)_2 \end{cases}$	From benzaldehyde and diethylaniline.

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Brown powder, red solution in hot water.	No change.	Yellow.	Yellow.	....	Soluble in alcohol.
Green metallic powder, violet solution.	Ppt.	First blue, then green, finally yellow.	Yellow.	Violet.	Basic dye. Soluble in alcohol.
Dark blue powder, blue solution.	Violet on warming.	Yellowish.	Yellow.	Green then blue	Acid dye for wood. Nitric acid (sp. gr. 1.40) yellow with greenish edge.
Dark blue powder. blue solution.	Red on boiling.	Yellow.	Yellow.	Blue after first turning yellowish-green.	Acid dye for wood.
Brown powder. Insoluble in water. In hot alcohol, blue solution.	....	....	Yellow.	Blue ppt.	Soluble in alcohol. Basic dye.
Coppery red-brown powder, blue solution.	Alteration slight.	Yellowish-green with concentrated acid. Only slightly affected by 10 % acid.	Light brown.	First light green then light blue.	Gives a reddish-yellow with nitric acid (sp. gr. 1.40). Not easily attacked by stannous chloride in hydrochloric acid. Used on wool.
Dark blue powder. bronzy lustre, greenish-blue solution.	Greener. Violet on boiling.	Yellow.	Pale yellow solution.	First green then greenish-blue.	Reddish-yellow with nitric acid (sp. gr. 1.40). Greener with stannous chloride in hydrochloric acid.
Golden crystals, green solution.	Decolourised and green ppt.	Orange.	Yellow.	Green after giving reddish-yellow and yellowish-green.	Basic dye. Soluble in alcohol. For silk, wool, jute, leather and cotton (tannin mordant).

Commercial name	Formula	Remarks
Ethyl Violet. Ethyl Purple 6B.	$C\begin{cases}(1)C_6H_4(4)N(C_2H_5)_2\\(1)C_6H_4(4):N(C_2H_5)_2Cl\\(1)C_6H_4(4).N(C_2H_5)_2\end{cases}$	....
Fast Acid Violet 10 B.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_3\begin{cases}(2)SO_3Na\\(4):N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_2.O\end{cases}\end{cases}\end{cases}$	....
Fast Green Fast Green extra (bluish).	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\(1)C_6H_4(4):N(CH_3)_2\\(1)C_6H_4(3)N\begin{cases}CH_2.C_6H_4.SO_2.O\\CH_2.C_6H_4.SO_3Na\end{cases}\end{cases}$	....
Fast Wool Green (Kalle).	....	....
Formyl Violet S 4B. Acid Violet 6 B and 4 B extra.	$C\begin{cases}(1)C_6H_4(4)N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_3Na\end{cases}\\(1)C_6H_4(4):N(C_2H_5)_2\\(1)C_6H_4(4)N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_2.O\end{cases}\end{cases}$	....
Glacier Blue.	$C\begin{cases}(1)C_6H_3\begin{cases}(3)CH_3\\(4)NH.CH_3\end{cases}\\(1)C_6H_3\begin{cases}(3)CH_3\\(4):NH(CH_3)Cl\end{cases}\\(1)C_6H_3\begin{cases}Cl(2)\\Cl(5)\end{cases}\end{cases}$	....
Guinea Green BV.	$C\begin{cases}(1)C_6H_5\\(1)C_6H_4(4)N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_3Na\end{cases}\\(1)C_6H_4(4):N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_2\end{cases}\end{cases}$ O	Condensation of benzaldehyde with ethyl-benzylaniline-sulphonic acid.
Helvetia Green.	$C\begin{cases}C_6H_4.SO_2.O\\(1)C_6H_4(4):N(CH_3)_2\\(1)C_6H_4(6)H(CH_3)_2\end{cases}$	Sulphonation of malachite green.
Höchst New Blue.	$C\begin{cases}(1)C_6H_4(4)N\begin{cases}CH_3\\C_6H_4.SO_3Na\end{cases}\\(2)C_6H_4(4):N\begin{cases}CH_3\\C_6H_4.SO_2.O\end{cases}\\(1)C_6H_4(4)N\begin{cases}CH_3\\C_6H_4.SO_3Na\end{cases}\end{cases}$	....

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. Acid	On dilution with water	
Green crystalline powder, Violet solution.	Violet ppt.	Orange.	Yellow.	Green.	Basic dye.
Gray powder, violet solution.	No change, pink on warming.	Citron yellow solution.	Orange.	Yellow, with much water green.	Acid dyestuff.
Dark blue-green crystalline powder. Greenish-blue solution.	Decolourised on warming.	Yellow.	Yellowish-red solution.	Almost colourless, with large dilution greenish-blue.	Dyes wool in acid bath.
Blue powder.	Somewhat lighter.	Yellower.	Orange.		Dyes wool a bluish-green. On the fibre gives the following reactions: Hydrochloric acid, yellower; sodium hydroxide, a little weaker; concentrated sulphuric acid, orange solution.
Violet powder. Violet solution.	Blue ppt. colourless on warming.	Violet ppt. Bright yellow with concentrated acid.	Orange.	Blue.	Acid dye. Bright green with stannous chloride in hydrochloric acid.
Violet powder. Greenish-blue solution, gelatinous on cooling.	Orange.	Yellow.	Yellow.	Green ppt.	Basic dye. Soluble in alcohol. For silk, wool, cotton (tannin mordant).
Green powder, green solution.	Blackish-green ppt.	Green ppt.	Brown.	Green.	Acid dye. Dyes silk and wool from an acid bath.
Green powder, bluish-green solution.	Decolourised	Brown ppt.	Yellow.	Green.	Obsolete. An acid dye.
Dark blue powder, blue solution.	Decolourised	Precipitate.	Red.	Blue ppt.	Acid dye.

Commercial name	Formula	Remarks
Hofmann Violet. Iodine Violet. Dahlia. Primula. Red Violet 5 R extra. Violet 5R, R and RR.	$C\begin{cases}(1)C_6H_4(4)NHC_2H_5\\(1)C_6H_4(4){:}NH(C_2H_5)Cl\\(1)C_6H_4\begin{cases}(3)CH_3\\(4)NHC_2H_5\end{cases}\end{cases}$	....
Iodine green Night Green Pomona Green. Vert lumière.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_3Cl\\(1)C_6H_4(4){:}N(CH_3)_2Cl\\(1)C_6H_4\begin{cases}(3)CH_3\\(4)N(CH_3)_2\end{cases}\end{cases}$	By prolonged alkylation of rosaniline.
Isorubine. New Magenta. New Fuchsine.	$C\begin{cases}(1)C_6H_4\begin{cases}(3)CH_3\\(4)NH_2\end{cases}\\(1)C_6H_4\begin{cases}(3)CH_3\\(4){:}NH_2Cl\end{cases}\\(1)C_6H_4\begin{cases}(3)CH_3\\(6)NH_2\end{cases}\end{cases}$	....
Ketone Blue 4 BN.	$C\begin{cases}(1)C_6H_4(3)OC_2H_5\\(1)C_6H_4(4)N(CH_3)_2Cl\\(1)C_6H_4(4)N\begin{cases}CH_3\\C_6H_5\end{cases}\end{cases}$	....
Light Green SF (Bluish). Acid Green. Acid Green M. Acid Green (Bluish).	$C\begin{cases}(1)C_6H_4(4)SO_3Na\\(1)C_6H_4(4)N\begin{cases}CH_3\\CH_2.C_6H_4.SO_2.O\end{cases}\\(1)C_6H_4(4).N\begin{cases}CH_3\\CH_2.C_6H_4.SO_2ONa\end{cases}\end{cases}$	From benzaldehyde and methyl-benzyl-aniline. Sulphonated and oxidised.
Light Green SF (Yellowish). Acid Green. Acid Green, extra conc. Acid Green D, etc.	$C\begin{cases}(1)C_6H_4(4)SO_3Na\\(1)C_6H_4(4){:}N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_2.O\end{cases}\\(1)C_6H_4(4).N\begin{cases}C_2H_5\\CH_2.C_6H_4.SO_3Na\end{cases}\end{cases}$	....
Magenta Roseïne. Fuchsine. Aniline Red, etc.	$C\begin{cases}(1)C_6H_4(4)NH_2\\(1)C_6H_4(4){:}NH_2Cl+4H_2O\\(1)C_6H_4\begin{cases}(3)CH_3\\(4)NH_2\end{cases}\end{cases}$	Mixed with pararosaniline.
Malachite Green. New Victoria Green New Green. Fast Green. Benzal Green. Diamond Green, etc.	$C\begin{cases}(1)C_6H_5\\(1)C_6H_4(4){:}N(CH_3)_2Cl+2ZnCl_2+2H_2O\\(1)C_6H_4(4)N(CH_3)_2\end{cases}$	Also as oxalate.

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Green crystalline powder, violet solution.	Brown ppt.	Yellow.	Brown.	Violet.	Basic dye.
Green, bluish-green solution.	Decolourised	Orange.	Orange.	Green.	Obsolete. Basic dye.
Green powder, red solution.	Red ppt.	Yellow.	Yellow.	Red.	Soluble in alcohol. Basic dye.
Red-violet lumps, blue solution.	Brown-red.	Decolourised.	Yellow.	Green.	
Brown-black powder, green solution.	Decolourised Violet ppt.	Yellow.	Yellow.	Green.	Acid dye. Sensitive to dilute alkali.
Green powder, green solution.	Decolourised Violet ppt.	Yellow.	Yellow.	Green.	Acid dye.
Green crystals, red solution.	Decolourised reddish ppt.	Yellow.	Brownish-yellow.	Colourless.	Basic dye. Soluble in alcohol. Absorption spectrum, band between D and E.
Green or yellow crystals, bluish-green solution.	Decolourised and greenish ppt.	Orange.	Yellow.	Green after giving first dark yellow, then yellow-green.	Basic dye. Soluble in alcohol. Precipitated by picric acid. Used on wool (which may first be mordanted with sodium thiosulphate) silk, jute, leather.

Commercial name	Formula	Remarks
Methyl Blue. Brilliant Cotton Blue. Bavarian Blue DB-F. Soluble Blue 8 B and 10 B. Helvetia Blue.	$C \begin{cases} (1)C_6H_4(4)NH.C_6H_4.SO_3Na \\ (1)C_6H_4(4) = NH.C_6H_4.SO_2 - O \\ (1)C_6H_4(4)NH.C_6H_4.SO_3Na \end{cases}$	....
Methyldiphenylamine Blue		
Methyl Green. Paris Green Light Green, etc.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4):N(CH_3)_2Cl + ZnCl_2 \\ (1)C_6H_4(4)N(CH_3)_3Cl \end{cases}$	Action of methyl chloride on methyl violet.
Methyl Violet B., 2 B, V3. Violet 3 B extra. Violet de Paris, etc.	$C \begin{cases} (1)C_6H_4(4)N(CH_3)_2 \\ (1)C_6H_4(4)N(CH_3)_2Cl \\ (1)C_6H_4(4)NH(CH_3) \end{cases}$	Oxidation of dimethylaniline.
Methyl Violet 6 B.		
New Victoria Blue A.		
Neutral Wool Blue R (Kalle).	....	....
Night Blue.	$C \begin{cases} (1)C_6H_4(4)N(C_2H_5)_2 \\ (1)C_6H_4(4):N(C_2H_5)_2Cl \\ (1)C_{10}H_6(4)NH.C_6H_4.CH_3 \end{cases}$	....
Night Blue B.		
Night green 2 B.	$C \begin{cases} (1)\ C_6H_4(2)Cl \text{ and } (1)C_6H_4 \begin{cases} (2)Cl \\ (5)NO_2 \end{cases} \\ = (1)C_6H_4(4):N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_2.O \end{cases} \\ (1)C_6H_4(4).N \begin{cases} C_2H_5 \\ CH_2.C_6H_4.SO_3Na \end{cases} \end{cases}$	From o-chloro-benzaldehyde (or o-chloro-m-nitro-benzaldehyde) and ethyl-benzylaniline sulphonic acid.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Dark blue powder, blue solution.	Brown.	No change.	Brown.	Blue.	
Green crystals, bluish-green solution.	Decolourised	Orange.	Orange.	Green.	Obsolete. Basic dye.
Green metallic powder, violet solution.	Brown ppt. and colour.	Brown.	Yellow.	Violet after going successively yellowish-green and green-blue.	Basic dye. Soluble in alcohol.
Dark blue powder.	....	....	....	....	Gives a pure blue on wool, dyed in acid or neutral bath. On the fibre hydrochloric acid, green; sodium hydroxide, weak dull red-brown; conc. Sulphuric acid, red solution.
Bronzy powder, bluish-violet solution.	Brown ppt.	Blue ppt. soluble in excess to brown solution.	Brown.	Blue.	Soluble in alcohol.
Blue-green powder, Blue-green solution.	Green ppt.	Green ppt.	Yellow.	Green pt.	Easily soluble in alcohol. The non-nitrated dye gives a redder solution in concentrated sulphuric acid.

Commercial name	Formula	Remarks
Pacific Blue		
Parafuchsin Para Magenta.	$C\begin{cases}(1)C_6H_4(4)NH_2\\(1)C_6H_4(4):NH_2Cl+4H_2O\\(1)C_6H_4(4)NH_2\end{cases}$	....
Patent Blue A.	$C\begin{cases}(1)\ C_6\ H_4\ (4)\ N\begin{cases}C_2H_5\\CH_2.C_6H_5\end{cases}\\(1)\ C_6\ H_4\ (4):N\begin{cases}C_2H_5\\CH_2.C_6H_5\end{cases}\\(1)C_6H_2\begin{cases}(2)SO_2.O\\(4)SO_3\tfrac{1}{2}Ca\\(5)OH\end{cases}\end{cases}$	....
Patent Blue V, N, extra, superfine. New Patent Blue Band 4B.	$C\begin{cases}(1)\ C_6\ H_4\ (4)\ N\ (C_2\ H_5)_2\\(1)\ C_6\ H_4\ (4):N\ (C_2H_5)_2\\(1)C_6H_2\begin{cases}(6)SO_2.O\\(4)SO_3\tfrac{1}{2}Ca\\(3)OH\end{cases}\end{cases}$	....
Phenolphthalein.	$C\begin{cases}(1)C_6H_4(4)OH\\(1)C_6H_4(4)OH\\C_6H_4.CO.O\end{cases}$	....
Red Violet 4RS. Acid Violet 4RS.	$C\begin{cases}(1)C_6H_3\begin{cases}(4)NH.CH_3\\(3)SO_3Na\end{cases}\\(1)C_6H_2\begin{cases}(3)CH_3\\\left.\begin{matrix}(4):NH_2\\(5).SO_2\end{matrix}\right>O\end{cases}\\(1)C_6H_3\begin{cases}(3)SO_3Na\\(4)NH_2\end{cases}\end{cases}$	....
Red Violet 5RS.	$C\begin{cases}(1)C_6H_3\begin{cases}(3)SO_3Na\\(4)NH.C_2H_5\end{cases}\\(1)C_6H_2\begin{cases}(3)CH_3\\\left.\begin{matrix}(4)NH_2\\(5)SO_2\end{matrix}\right>O\end{cases}\\(1)C_6H_3\begin{cases}(3)SO_3Na\\(4)NH_2\end{cases}\end{cases}$	....
Regina Purple.	$C\begin{cases}(1)C_6H_4(4)NH.C_6H_4.CH_3\\(1)C_6H_4(4):NH_2Cl\\(1)C_6H_4(4)NH_2.\end{cases}$	By-product in manufacture of magenta.
Rosolic Acid.	$C\begin{cases}(1)C_6H_4(4)OH\\(1)C_6H_4(4):O\\(1)C_6H_3\begin{cases}(3)CH_3\\(4)OH\end{cases}\end{cases}$	Mixed with aurine which it resembles.
Setocyanine Brilliant Glacier Blue.	$C\begin{cases}(1)C_6H_4(2)Cl\\(1)C_6H_3\begin{cases}(3)CH_3\\(4):NH(C_2H_5)Cl\end{cases}\\(1)C_6H_3\begin{cases}(3)CH_3\\(4).NH.C_2H_5\end{cases}\end{cases}$	From *o*-chlorobenzaldehyde and ethyl-*o*-toluidine.

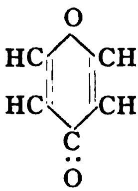
Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Green crystals, red solution.	Reddish ppt.	Yellow.	Yellow.	Colourless.	Basic dye. Soluble in alcohol.
Copper red powder, blue solution.	Violet on heating.	Green with precipitation of colour acid.	Yellow.	Green with precipitation of colour acid.	Acid dye for wool.
Copper red powder, blue solution.	No change in cold, violet when boiled.	Green, yellow.	Yellow.	Green.	Acid dye.
....	Pink, decolourised on standing or heating with excess of soda.	Precipitated colourless.			
Violet powder, violet solution.	Orange.	No change.	Yellow.	Violet.	Acid dye. Very sensitive to sodium hydroxide and ammonia.
Violet metallic lumps, violet solution.	Yellow.	No change.	Yellow.	Violet.	Acid dye. Colours wool bluish-red from an acid bath.
Green powder, violet solution.	Brown ppt.	Brown, blue on dilution.	Brown.	First brown then blue.	
Gray-green powder. Soluble in hot water (greenish blue).	Brown ppt.	Yellow.	Reddish-yellow.	Green.	Sparingly soluble in cold water, the hot solution cools to a jelly. Easily soluble in alcohol. For silk and cotton (tannin mordant).

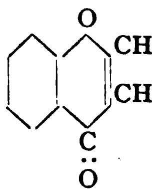
Commercial name	Formula	Remarks
Setoglaucine. New Fast Green 3B.	$C\begin{cases}(1)C_6H_4(2)Cl\\ (1)C_6H_4(4){:}N(CH_3)_2Cl\\ (1)C_6H_4(4).N(CH_3)_2\end{cases}$	Condensation of *o*-chlorobenzy-aldehyde with dimethylaniline. Subsequently oxidised.
Soluble Blue. Water Blue China Blue. Cotton Blue	$C\begin{cases}(1)C_6H_3\begin{cases}(3)CH_3\\ (4)NH.C_6H_4.SO_3Na\end{cases}\\ (1)C_6H_4(4)=NH.C_6H_4.SO_2\\ (1)C_6H_4(6)NH.C_6H_4.SO_3Na\end{cases}$	
Soluble Blue XG.		Condensation of β-Naphthyl amine with rosaniline and subsequent sulphonation.
Soluble Regina Violet	....	Sulphonation of Spirit Violet.
Spirit Blue. Aniline Blue Spirit soluble. Gentian Blue 6B. Hessian Blue. Bleu de nuit, etc.	$C\begin{cases}(1)C_6H_4(4)NH.C_6H_5\\ (1)C_6H_4(4){:}NH(C_6H_5)Cl\\ (1)C_6H_4\begin{cases}(3)CH_3\\ (4)NHC_6H_5\end{cases}\end{cases}$	By phenylation of rosaniline by heating with aniline.
Spirit Violet.	? Hydrochloride of diphenylrosaniline.	....
Victoria Blue B, BS.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ (1)C_6H_4(4){:}N(CH_3)_2Cl\\ (1)C_{10}H_6(4)NH.C_6H_5\end{cases}$	Condensation of phenyl-α-naphthylamine with Michler's hydrol.
Victoria Blue R. New Victoria Blue R.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ (1)C_6H_4(4){:}N(CH_3)_2Cl\\ (1)C_{10}H_6(4)NHC_2H_5\end{cases}$	....
Victoria Blue 4 R.	$C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ (1)C_6H_4(4){:}N(CH_3)_2Cl\\ (1)C_{10}H_6(4)N\begin{cases}CH_3\\ C_6H_5\end{cases}\end{cases}$	....
Victoria Green 3 B. New Fast Green 3 B.	$C\begin{cases}(1)C_6H_3Cl_2(2\text{ and }5)\\ (1)C_6H_4(4){:}N(CH_3)_2Cl\\ (1)C_6H_4(4)N(CH_3)_2\end{cases}$	....
Wool Green S.	? $C\begin{cases}(1)C_6H_4(4)N(CH_3)_2\\ (1)C_6H_4(4){:}N(CH_3)_2\\ C_{10}H_5\begin{cases}SO_2-O\\ OH\end{cases}\end{cases}$	....

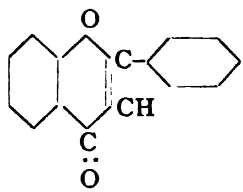
Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics.
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Copper-red powder, blue-green solution.	Blue-black ppt. which soon turns red-brown.	Reddish-yellow colour.	Reddish-yellow solution.	First turns yellow, more water causes it to go green	Easily soluble in alcohol. For silk and cotton (tannin mordant).
Blue coppery powder, blue solution.	Brown.	Slight ppt.	Orange.	Blue ppt.	Acid dye.
Flakes, reddish metallic lustre.	Dull claret.	Blue ppt.	Reddish Brown.	Blue ppt.	Acid dye.
Bronze powder, violet solution.	Lighter.	Violet ppt.	....	....	Acid dye.
Bronzy powder. Insoluble.	Brown.*	No change.*	Yellow.	Blue ppt.	Basic dye. Soluble in alcohol. *Reaction of alcoholic solution.
....	....	....	Brown.	Violet ppt.	Basic dye. Soluble in alcohol.
Bronzy powder, blue solution.	Brown ppt.	Blue ppt. Soluble in excess. Red	Orange-red.	Blue after first going yellow and green.	Soluble in alcohol. Nitric acid (sp. gr. 1.40); greenish-yellow with red edge. Stannous chloride in hydrochloric acid; darker.
Blue powder, blue solution.	Brown ppt.	Brown solution.	Yellowish-brown solution.	Bright green then blue.	Basic dye. Soluble in alcohol.
Bronzy powder, violet solution.	Brown ppt.	Blue ppt. Red with concentrated acid.	Red-brown.	Blue.	Nitric acid (sp. gr. 1.40); greenish yellow with brown edge.
Green crystals, greenish-blue solution in hot water, gelatinises on cooling.	Orange and slight precipitate.	Yellow.	Yellow.	Green.	Basic dye. Soluble in alcohol. For silk, wool and cotton (tannin mordant.)
Violet powder, green solution.	Bluer. On warming violet, then pink.	Yellow.	Brown-violet solution.	Green.	Soluble in alcohol. Only slight-ly altered by stannous chloride in hydrochloric acid

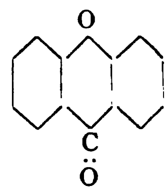
7. PYRONE, XANTHONE AND FLUORAN DYES.

Many dyestuffs are characterised by the presence of a pyrone ring in the molecule; of the 6 members of this ring, 5 are carbon atoms and the remaining member an oxygen atom. Pyrone itself is a colourless compound, but when situated adjacent to 1, or between 2 aromatic nuclei, as in chromone and xanthone, the introduction of auxochromic groups in suitable positions gives rise to a number of dyestuffs.


Pyrone.

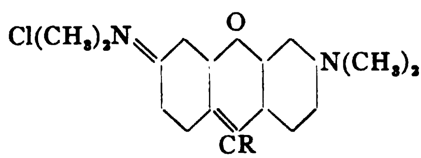

Chromone.

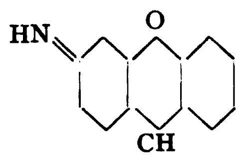

Flavone.

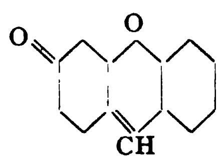

Xanthone.

Among the structures involving the pyrone ring, chromone, flavone and xanthone may be specially mentioned. Many naturally occurring dyestuffs are hydroxylic derivatives of the two latter compounds, while the artificial dyestuffs of the series are almost without exception genetically related to xanthone.

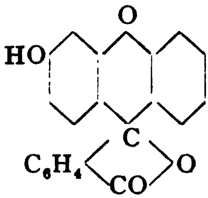
The pyronines (I) are derived from fluorime (II) and related to fluorone (III)


I

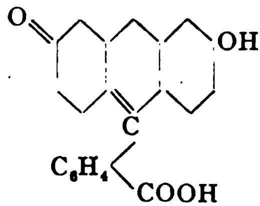

II


III

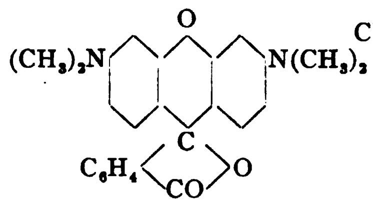
while fluoresceïn (IV and IVa) and its derivatives and the rhodamines (an example is given by V and Va) may be considered



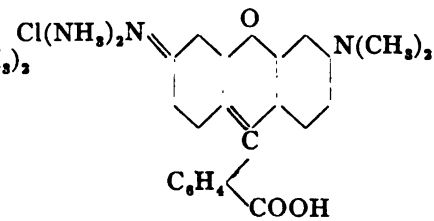
IV



IVa

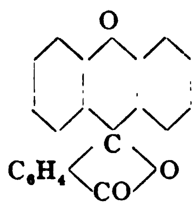


V



Va

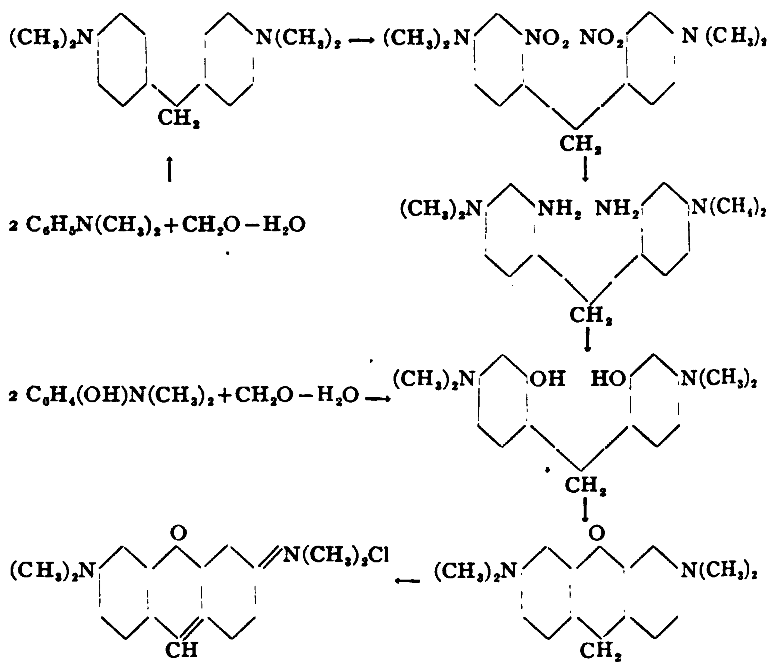
as derived either from fluorone and fluorime respectively or from a parent substance fluoran (phenolphthaleïn anhydride)



according to which of the tautomeric formulæ is taken. It seems probable that an alkaline solution of fluoresceïn contains salts which pass between the 2 forms corresponding with formulæ IV and IVa, for Nietzki and Schroeter (*Ber.*, 1895, **28**, 44) obtained on alkylation a colourless lactonoid diethyl-ether and an isomeric yellowish-red quinonoid ether-ester at the same time. An oscillation of the molecules of fluoresceïn between the 2 structures IV and IVa has been suggested by Hewitt (*Zeitsch. physikal. Chem.*, 1900, **34**, 5) in explanation of the fluorescence of solutions of this compound.

Pyronine and its Derivatives.

Pyronine G or **Casan Pink** (Gerber) may be obtained either from dimethylaniline and formaldehyde or from the latter compound and dimethyl-*m*-aminophenol. In the former case the 2 substances are condensed to tetramethyl-*p*-diaminodiphenylmethane which is then nitrated and reduced. The resulting tetra-amino-compound is then diazotised and boiled with water yielding tetramethyl-*pp*-diamino-*oo*-dihydroxydiphenylmethane, a substance which may also be produced by the direct condensation of formaldehyde and dimethyl-*m*-aminophenol. Water is eliminated by means of sulphuric acid and the leuco-compound oxidised:



Pyronine G is a red dyestuff somewhat resembling the rhodamines in shade. It occurs in the form of green crystals, soluble in water, giving a red solution having a yellow fluorescence; also soluble in alcohol with a red colour and a yellow fluorescence. On treating the aqueous solution with sodium hydroxide a pale red precipitate is

produced; the addition of excess of hydrochloric acid causes the colour of the aqueous solution to become bright orange. With strong sulphuric acid the dyestuff gives an orange solution, which becomes red on dilution with water.

There is a corresponding tetra-ethyl derivative which is called Pyronine B; its shade is somewhat bluer than the preceding compound, and its fluorescence is redder, otherwise its reactions are similar to those described for Pyronine G. The pyronines dye cotton mordanted with tannic acid brilliant bluish-red shades.

Acridine red 3 B (also B, and BB) is obtained by the oxidation of pyronine B by means of potassium permanganate. It possibly has the formula:

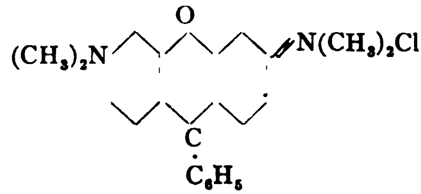
$$
\begin{array}{lllll}
 & & & & {/\!\!/}N(Cl)(C_2H_5)_2 \\
 & & {/\!\!/}C_6H_3 & \!\!\!\diagup & \\
HO.C & \!\!\!\diagup\!\!\!\diagdown & & \!\!\!> O & \\
 & & \diagdown C_6H_3 & \!\!\!\diagdown & \\
 & & & & \diagdown N(C_2H_5)_2
\end{array}
$$

It is a brown powder soluble in water and alcohol, giving a red solution with a yellow fluorescence. Sodium hydroxide added to the aqueous solution produces a red precipitate; the addition of hydrochloric acid changes the colour to orange. With strong sulphuric acid the dyestuff gives a yellow solution with a green fluorescence; dilution with water causes the colour to change to red.

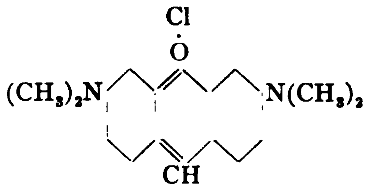
Acridine red is dyed with a tannin mordant on either cotton or silk in a manner similar to the pyronines, but the shade obtained is more yellow than that produced by the latter. The colour is quite fast to washing and light.

By the action of a solution of sulphur in fuming sulphuric acid (sulphur sesquioxide) on tetramethyldiaminodiphenylmethane, Sandmeyer obtained a strongly fluorescent dyestuff analogous to pyronine but containing a sulphur atom in place of the oxygen atom of the pyrone ring. (J. R. Geigy and Co., German patent 65,739.)

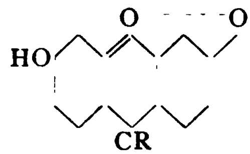
When dimethyl-*m*-aminophenol is condensed with benzotrichloride, a dihydroxyl-derivative of malachite green is probably first produced; it loses water, however, passing into a dyestuff *Rosamine*, which is simply a phenyl-derivative of pyronine; its structure is given by the formula:



It should be mentioned that Kehrmann advocates an oxonium formula (I) for the dyestuffs of this class,

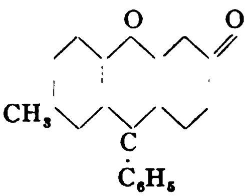


I

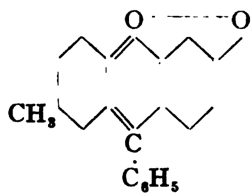


II

while the corresponding formula (II) which he (*Ber.*, 1908, **41**, 3441) assigns to the hydroxyfluorones, seems quite untenable. (Kropp and Decker, *Ber.*, 1909, **42**, 578.) F. G. Pope and H. Howard who have prepared a fluorone to which either the structure III or IV must be assigned



III



IV

find that it is not dissolved by alkalies which renders an oxonium-phenol-betaine formula very improbable. (*Trans. Chem. Soc.*, 1910, **97**, 1023.)

Fluorescein, $C_{20}H_{12}O_5$, results from the condensation of phthalic anhydride and resorcinol. It is prepared by heating 3 parts of phthalic anhydride and 4 of resorcinol to 200°–210° for 1 hour, or till no more steam is evolved and the melt has become solid. The product is purified by solution in sodium hydroxide and addition of

sodium phosphate and calcium chloride to the solution, when the phosphate of calcium carries down the impurities, and the fluoresceïn may be precipitated by acidifying the filtrate.

Fluoresceïn forms an amorphous yellow precipitate which becomes crystalline and yellowish-red on standing or drying, and then contains $C_{20}H_{12}O_5+H_2O$. It is nearly insoluble in cold water, more readily in acidified, and sparingly in hot water, to which it imparts a yellow colour. When freshly precipitated it dissolves readily in alcohol and ether, but is nearly insoluble in benzene and chloroform. The ethereal solution is pale yellow and non-fluorescent, while the yellowish-red alcoholic solution shows a green fluorescence.

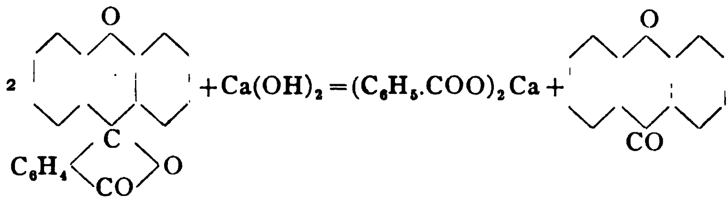
Fluoresceïn is a feeble acid, dissolving in alkalies with dark red colour. The strong alkaline solution is not fluorescent, but on dilution it changes to reddish-yellow and yellow, and then exhibits a magnificent yellowish-green fluorescence, similar to that of uranium glass, and gives an absorption-spectrum with a broad dark band in the green. Even if the solution be so dilute as to appear colourless by transmitted light, the green bloom is still visible.

When a solution of fluoresceïn in aqueous sodium hydroxide is heated with zinc-dust the liquid becomes colourless and contains *fluorescin*, $C_{20}H_{14}O_5$. On filtering from the excess of zinc and exposing the liquid to the air, it gradually re-acquires its reddish colour, owing to the absorption of atmospheric oxygen and re-formation of fluoresceïn. Or if the colourless liquid be acidified and agitated with ether, the fluoresceïn is dissolved, and on evaporating the ether is left as a colourless varnish, soluble without colouration in sodium hydroxide, giving a liquid which rapidly turns red in the air from formation of fluoresceïn. The oxidation is immediate on addition of a ferricyanide to the alkaline liquid.

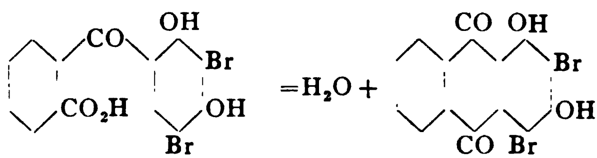
Fluoresceïn dyes silk and wool yellow, but the colours are not fast. It forms insoluble lakes with silver, lead, etc., which compounds are not poisonous, and hence may be used for colouring toys, india-rubber goods, etc.

Besides its feebly acid properties fluoresceïn can exercise weak basic functions, giving salts which are to be regarded as of oxonium type. (Baeyer, *Annalen*, 1876, **183**, 27; Hewitt and Tervet, *Trans.*, 1902, **81**, 665.) Similar salts with acids may be obtained from its colourless diethyl ether (Nietzki and Schroeter, *Ber.*, 1895, **28**, 56) and the parent substance fluoran. (Hewitt and Tervet, *Loc. Cit.*).

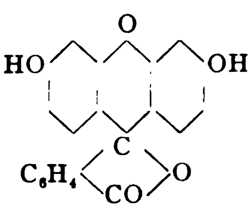
The constitution assigned to fluoresceïn has been confirmed by its conversion into fluoran or phenolphthaleïn anhydride (R. Meyer, *Ber.*, 1891, **24**, 1412; 1892, **25**, 1385; 1895, **28**, 428); which when distilled with lime gives calcium benzoate and xanthone:

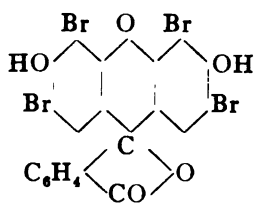


The position of the hydroxyl groups is rendered certain by the fact that the dibromodihydroxybenzoylbenzoic acid obtained from eosin (tetrabromofluoresceïn) by the action of alkalies and reconvertible into the latter substance by elimination of phthalic anhydride by direct heating (R. and H. Meyer, *Ber.* 1896, **29**, 2623) may be condensed directly to a dibromodihydroxyanthraquinone of known constitution (Heller, *Ber.*, 1895, **28**, 312)



consequently fluoresceïn and eosin must possess the respective formulæ,





or have equivalent tautomeric quinonoid constitutions.

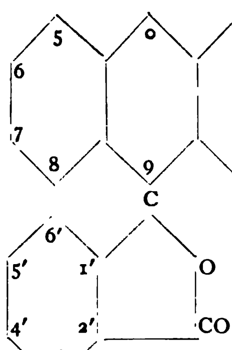
Chrysolin (sometimes called uranin), obtained by condensing benzylresorcinol and phthalic acid in presence of strong sulphuric acid and conversion of the product into the sodium salt, is a reddish-brown powder possessing a greenish reflex. Its aqueous and alcoholic solu-

tions are yellowish-brown, and exhibit a remarkable green fluorescence, which disappears with formation of a brown-yellow precipitate of benzylfluoresceïn on addition of acids. The precipitate is soluble in ether. The aqueous solution is darkened by alkalies, and the solid dye dissolves in strong sulphuric acid with yellow colour, and yields a yellow precipitate on dilution. With stannous chloride and with lead salts, chrysolin gives brilliantly coloured lakes. It dyes silk or wool a fast yellow, and is employed in cotton-dyeing for topping quercitron-yellow, the quercitron itself acting as a mordant.

Substitution Derivatives of Fluorescein.

Substitution derivatives of fluoresceïn may be obtained by the condensation of substituted phthalic anhydrides with resorcinol or by the action of substituting reagents (halogens, nitric acid) on fluoresceïn, or by combining the two processes. In acting upon fluoresceïn with bromine or nitric acid, dissubstituted derivatives are first produced and eventually tetrasubstituted compounds.

If the positions in the parent substance fluoran be numbered according to the scheme



fluoresceïn may be described as 3:6-dihydroxyfluoran, and it has been shown that positions 4 and 5 are those first attacked on substitution, the hydrogen atoms at 2 and 7 being replaced subsequently (L. Matras, *Chem. Zeit.*, 1895, **19**, 408; *Arch. Sci. phys. nat.*, 1895, [iii], **33**, 285; Hewitt and Woodforde, *Trans. Chem. Soc.*, 1902, **81**, 893). Compounds containing nitro-groups in positions 4 and 5 easily

take up a molecule of water, 4 : 5-dinitrofluoresceïn for instance dissolving in dilute alkalies with a brown colour (pyrone ring intact) which passes into blue on warming. This colour passes into a dirty shade of brown on continued warming, a molecule of nitroresorcinol being eliminated from the dinitrofluoresceïn molecule.

Nitro-groups in positions 4 and 5 are easily displaced by halogen, but not those in 2 and 7. The statements which are sometimes met with that the same dibromo-dinitrofluoresceïn results from the bromination of dinitrofluoresceïn and the nitration of dibromofluoresceïn as well as from the reaction between tetrabromofluoresceïn and nitric acid (or tetranitrofluoresceïn and bromine) are obviously incorrect. Hewitt and Woodforde (*loc. cit.*) definitely established the following relationships:

$$\text{Fluoresceïn}\begin{cases}\nearrow \text{4:5-Dinitrofluoresceïn} \longrightarrow \text{2:7-dibromo-4:5-dinitrofluoresceïn.}\\ \searrow \text{4:5-Dibromofluoresceïn} \longrightarrow \text{4:5-dibromo-2:7-dinitrofluoresceïn.}\end{cases}$$

4 : 5-Dinitrofluoresceïn and its 2 : 7-dibrominated derivative dissolve in cold dilute alkalies with a brown shade passing into blue on warming; from the blue solutions acids precipitate compounds containing the elements of 1 molecule of water in excess of that in the original substances, and these precipitates dissolve with immediate blue colour in cold dilute alkalies. These hydrated compounds (derivatives of phenolphthaleïn) are readily converted into the original fluoran derivatives by crystallisation from boiling acetic acid. The opening of the pyrone ring by warming with dilute alkalies does not occur in the case of 4 : 5-dibromofluoresceïn, eosin, or 4 : 5-dibromo-2 : 7-dinitrofluoresceïn.

Nitrated fluoresceïns containing more than 2 nitro-groups in the molecule do not give a blue colouration on warming with alkalies.

Tetrabromfluorescein, or **acid eosin,** $C_{20}H_8Br_4O_5$, is prepared by gradually adding 24 parts of bromine to 10 parts of fluoresceïn dissolved in 8 times its weight of strong alcohol. When half the bromine has been added, the product changes from reddish-brown to a very dark brown colour. This marks the formation of the dibromoderivative, which is easily soluble in alcohol. On continuing the addition of bromine the tetrabromfluoresceïn separates as a brick-red crystalline precipitate, which is washed with a little alcohol and then with water. An

alternative method of preparation is to mix a solution of fluoresceïn in sodium hydroxide with a solution of the calculated amount of bromine in sodium hydroxide, and then acidify the liquid with hydrochloric acid, when the tetrabromfluoresceïn is precipitated.

Tetrabromfluoresceïn closely resembles fluoresceïn itself. It is nearly insoluble in water, and its reddish-yellow solution in alcohol is not fluorescent (distinction from fluoresceïn). It is a well-defined dibasic acid, the salts of which are decomposed by mineral acids, but only imperfectly by acetic acid.

By cautious treatment with potassium hydroxide, acid eosin yields the potassium salt, $C_{20}H_6Br_4O_5K_2+6H_2O$, which is known in commerce as *Soluble Eosin*, and forms a red powder or brownish-red crystals with blue or yellowish-green reflection. It is not easily soluble in absolute alcohol, but dissolves completely in 2 or 3 times its weight of water to form a reddish-yellow solution. This on dilution becomes rose-coloured and exhibits an intense yellowish-green fluorescence, which is rendered still stronger by the addition of alcohol. The absorption-spectrum shows a broad dark band in the green, destroyed by mineral acids, but not by acetic acid. On adding hydrochloric acid the solution becomes yellow, and on heating gives a yellow precipitate of tetrabromfluoresceïn, which may be extracted by ether and removed from the ethereal solution by agitation with an alkali.

The sodium salt of the tetrabromfluoresceïn is an article of commerce under the name of *Eosin C*,[1] or in the form of garnet-red crystals as *Eosin B extra*. It closely resembles the potassium salt. The ammonium salt, known as *Eosin B*, of a *red* appearance, is prepared by the direct action of ammonia gas on tetrabromfluoresceïn.[2]

By the addition of a soluble salt of eosin to solutions of the heavy metals, sparingly soluble or insoluble lakes are obtained as precipitates. Silver gives red, and zinc, cobalt, iron, manganese, bismuth, and tin reddish-yellow lakes.

A bright vermilion lake may be obtained by mixing the solution of eosin with starch or kaolin and precipitating with alum. If excess of alkali be previously added to the solution, the precipitate obtained is carmine-red, and with still more alkali a pink lake results. From yellowish shades sulphate of zinc or magnesium should be used in conjunction with alum.

[1] Also known as: *Eosin yellowish, Eosin GGF, Water Soluble Eosin, Eosin A, Eosin 3J, and Eosin 4J, Eosin KS, Eosin DH, and Eosin JJF.*

[2] *Eosin Orange, Eosin 3G, Salmon Pink*, etc., are mixtures of di- and tetra-bromfluoresceïn.

Vermilionette is a brilliant lake obtained by precipitating eosin by lead acetate. Lighter shades are obtained by also adding sodium carbonate. A very bright vermilion-coloured product is obtained by stirring up red-lead with an alkaline solution of eosin and then adding lead acetate to complete precipitation. Basic chromate of lead (chrome-red) gives even a brighter red than red-lead. Vermilionette sometimes contains a considerable proportion of barium sulphate or other diluent.

Tetraiodofluorescein, or **iodeosin,** $C_{20}H_8I_4O_5$, is prepared by mixing solutions of fluoresceïn and iodine in sodium hvdroxide, and then adding acetic acid. Its alkaline salts are sold as *Eosin Blue-Shade* (soluble in water), *Eosin J*, *Erythrosin*, *Erythrosin B*, *Pyrosin B*, *Iodeosin B*, *Dianthin B*, *Soluble Primrose*, and *Erythrosin D*.[1] The sodium salt is brown-red and the ammonium salt light brick-red. Their aqueous solutions are not fluorescent (distinction from the brominated eosins), and on treatment with zinc-dust and ammonia the iodine is eliminated and a colourless solution of fluoresceïn obtained, turning red on exposure to air, with formation of fluoresceïn. *Erythrosin G* is the sodium or potassium salt of di-iodofluoresceïn.

Dibromo-dinitro-fluorescein is obtained technically by acting on an alcoholic solution of dibromofluoresceïn with nitric acid (Nietzki). It is a fairly strong dibasic acid sparingly soluble in alcohol and acetic acid but readily soluble in alkalies with a crimson shade; the solution shows no fluorescence. The diacetyl and dibenzoyl derivatives are colourless and melt at 215° and 301° (with decomposition) respectively. The salts are known in commerce as *Safrosin*, *Eosin Scarlet*, *Daphnin*, *Eosin BN*, *Methyl Eosin*, *Eosin Scarlet B*, *Eosin B*, *Scarlet J*, *JJ*, *and V*, *Nopalin*, *Eosin Scarlet BB*, *Eosin BW*, *Imperial Red*, *and Eosin DHV*. The potassium and sodium salts are dark brown or green powders, while the ammonium salt is red. A mixture of bromonitro-fluoresceïn with the di- and tetra-nitro-derivatives is known as *lutécienne*. *Rubeosin* is a nitrochlorofluoresceïn, obtained by the action of nitric acid on *Aureosin*, which is itself a chlorinated fluoresceïn.

Tetrabromo-dichlorofluorescein, $C_{20}H_6Cl_2Br_4O_5$.—In all the substituted fluoresceïns hitherto described the replaced hydrogen belongs to the resorcinol residue, but eosins may also be prepared in which the hydrogen atoms of the phthalic acid residue are replaced. Thus when dichlorophthalic acid acts on resorcinol a dichlorofluo-

[1] Some of these names are applied to the alkaline salts of a di-iodfluoresceïn, $C_{20}H_{10}I_2O_5$.

rescein is obtained, and by brominating or iodinating this substance other colouring matters result. *Rose Bengale*[1] and *Phloxin*[2] are dyes of this kind, the former being the potassium or sodium salt of tetraiododichlorofluoresceïn, and the latter the potassium salt of tetrabromodichloro- (or tetrachloro-) fluoresceïn. *Cyanosin* is the potassium salt of the methyl or ethyl ester of phloxin. *Phloxin TA* (*Eosin* 10 *B*, *Erythrosin B*) is the sodium salt of tetrabromtetrachlorfluoresceïn.

Esters of Substituted Fluoresceins.—The methyl and ethyl esters of tetrabromfluoresceïn are obtained by heating eosin with methyl or ethyl alcohol and sulphuric acid, by heating acid eosin with methyl or ethyl bromide, or by brominating fluoresceïn in hot alcohol, when esterification and bromination occur simultaneously. The potassium salt of ethyl-tetrabromfluoresceïn is a red crystalline substance with a greenish reflex. It has found a considerable application in silk-dyeing, and is known as *Spirit-eosin*, *Ethyl-eosin*, *Rose JB.*, *Spirit Primrose*, *Eosin BB*, *Eosin S*, etc. *Methyl-eosin* is of very similar character.

Methyl- and ethyl-eosin are sparingly soluble in water and insoluble in absolute alcohol, but they dissolve easily in proof-spirit, the dilute solutions having a beautiful fluorescence.

Reactions of the Eosins.—The halogen derivatives of fluoresceïn give solutions which fluoresce more feebly than fluorescein itself, the introduction of nitro-groups inhibiting the fluorescence completely. The absorption spectra of these substances has engaged the attention of C. H. Bothamley, (*J. Soc. Chem. Ind.*, 1887, **6**, 423) and J. Formànek (*Spektroskopischer Nachweis künstlicher organischen Farbstoffe*). The commercial eosins are usually soluble alkaline salts; from their aqueous solutions hydrochloric acid precipitates the free substituted fluoresceïns. In all cases the precipitates are soluble in ether, and on agitating the separated ethereal solution with sodium hydroxide or ammonia the eosin passes into the alkaline liquid with characteristic colour, and usually with fluorescence. On reduction the eosins readily give leuco-compounds. R. Benedikt (*Chemiker Zeitung*, 1883, **7**, 57) carried this out by shaking a dilute ammoniacal solution in the cold with zinc dust; all eosins are rapidly decolourised by this treatment. If the solutions be filtered they do not re-oxidise very rapidly (see Green, *J. Soc. Chem. Ind.*, 1893, **12**, 3); in most cases they pass back eventually to the

[1] Known also as *Rose Bengale, N., AT. G.*
[2] Known also as *Phloxin P, Erythrosin BB*, and *New Pink*.

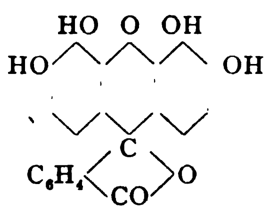
original eosin, but in the case of Eosin J (Iodoeosin) iodine is replaced by hydrogen and the colourless fluoresceïn solution obtained on reduction, when oxidised shows the powerful green fluorescence of fluoresceïn itself. The original colour is not obtained in the case of Safrosin (dinitro-dibromofluoresceïn), the nitro-groups being reduced to amino-groups. The colourless solution obtained in this case oxidises again with considerable rapidity, giving a cherry-red, non-fluorescent solution.

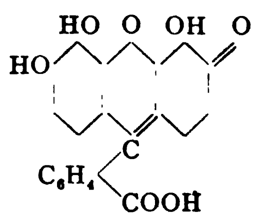
Aurin and its allies present a somewhat close analytical resemblance to the eosins; but their ammoniacal solutions are not fluorescent, and no bromine or iodine vapours are evolved on heating the substance with sulphuric acid and manganese dioxide.

The eosins produce on silk and wool all shades of colour from a reddish-orange to a cherry-red and purple. The yellowish shade is produced by Eosin G, and the bluest by Bengal Red. For dyeing cotton with eosins, the fabric is mordanted with alumina or tin for yellow shades, and with lead salts for blue shades. The colours produced are not so fast as those on wool or silk, and are affected by light.

The eosins soluble in water are slightly removed when *fibres* dyed with them are treated with warm water, especially if a little ammonia be added. Spirit-soluble eosins are not affected by water, but are dissolved from the fibre by alcohol, which leaves the eosins soluble in water.

Phthaleins of Other Phenols.—Phthalic anhydride may be condensed with many other polyhydric phenols yielding hydroxy-derivatives of fluoran which are, for the most part, of no great technical importance. By heating, however, with gallic acid at 200°, the latter loses carbon dioxide and galleïn, a condensation product of the resulting pyrogallol, is obtained. Like fluoresceïn, this substance may be regarded either as a fluoran derivative or as possessing a quinonoid structure:

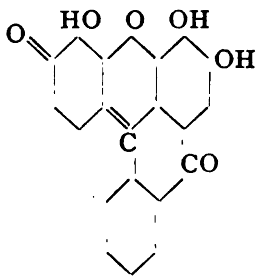




Its alkaline salts dissolve in water with a red colour; excess of alkali causes the solution to turn blue. The dyestuff gives insoluble, greyish-violet aluminium and chromium lakes; it is used for printing with the acetates of these two metals, the acetic acid being subsequently removed by steaming.[1]

Coerulein.—This dyestuff is produced by heating galleïn with 20 times its weight of concentrated sulphuric acid to 200° and pouring into water. It is almost insoluble in water, alcohol and ether, but dissolves somewhat with a green colour in glacial acetic acid, easily with olive-green colour in strong sulphuric acid, and with a blue shade in hot aniline.

Coeruleïn differs from galleïn by the elements of water and as it yields phenylanthracene on distillation with zinc dust, Orndorff and Brewer (*Am. Chem. J.*, 1899, **23**, 430) have assigned to it the constitution:



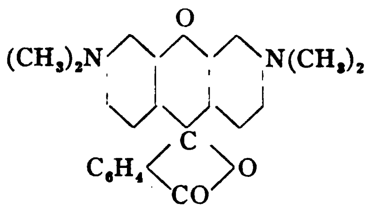
Coerulein S or SW is soluble in water and obtained from coeruleïn by combination with sodium hydrogen sulphite.

An isomer of galleïn which colours alumina mordants a fine red has been obtained by Feuerstein and Liebermann by the condensation of phthalic anhydride with 1:2:4-trihydroxybenzene (*Ber.*, 1901, **34**, 2299, 2637).

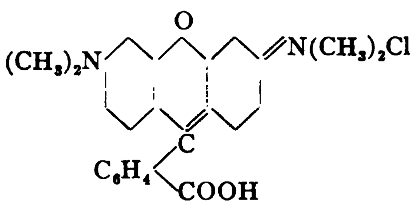
Rhodamines and Anisolines.—Whereas fluoresceïn and its derivatives, although capable of weak basic (oxonium) function, are chiefly characterised by acidic character, well marked basic dyestuffs are obtained by the condensation of phthalic and other similar anhydrides with *m*-aminophenol and its derivatives. These compounds,

[1] Galleïn like fluoresceïn, forms salts with a number of mineral acids and when these are decomposed by water, galleïn hydrate, $C_{20}H_{12}O_7H_2O$, is obtained. G. Heller has used these properties as a ready means of purifying the commercial dyestuff (*Zeit. Farben-Ind.*, 1906, **5**, 265).

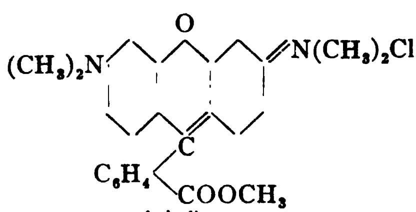
which give magnificent red shades and have very largely displaced the eosins, may also be obtained from fluoresceïn by conversion of the latter into its dichloride and subsequent reaction with dialkylamines. The rhodamines may be written either with a diamino-fluoran or with a quinonoid carboxylic structure; the latter seems the more probable in the salts at any rate since on heating a rhodamine chloride with an alcohol a carboxylic ester is produced. The first of these esters was introduced by Monnet under the name of "Anisoline." He attributed, however, an incorrect structure to the substance he had obtained. The structures of typical rhodamines and anisolines may be shown by the following formulæ:



(?)Free rhodamine base.



Rhodamine salt.



Anisoline.

The rhodamines and anisolines are thus represented as carboxylic acids and esters respectively of dyestuffs of rosamine type.

Mixed rhodamines or substances intermediate between rhodamines and fluoresceïns have been obtained by the Bindschedler Company of

Basel, by condensing equimolecular quantities of phthalic anhydride and alkylated *m*-aminophenols to derivatives of benzoylbenzoic acid and then allowing the latter substances to react with a second molecule of a different *m*-aminophenol or a phenol, the mixed dyestuffs obtained in the latter case being known as rhodines.

The Violamines are acid dyestuffs of this series; they are obtained by the condensation of fluoresceïn chloride with aniline or other aromatic bases and subsequent sulphonation; they are useful dyestuffs for wool.

The anhydride of practically any dicarboxylic acid of grouping

$$\begin{array}{l} \cdot\dot{C}—CO\diagdown \\ \;| \qquad\qquad\;\; \rangle O \\ \cdot\underset{\cdot}{C}—CO\diagup \end{array}$$

will condense with *m*-amino-phenols to give rhodamines; **Rhodamine S,** which gives a beautiful red on wool, is obtained from succinic anhydride.

The rhodamines generally dissolve in concentrated sulphuric acid with a yellow colour, the red shade being restored on dilution.

Commercial name	Formula	Remarks
Acridine Red B, 2B, 3B.	$? \; C(OH)\begin{array}{l} \diagup (1)C_6H_3 \diagup (4)N(C_2H_5)_2Cl \\ \qquad\qquad\quad O \\ \diagdown (1)C_6H_3 \diagdown (4)N(C_2H_5)_2 \end{array}$	By oxidation of pyronine B.
Chrysolin.	$\begin{array}{l} \quad (1)C_6H_2\left\{\begin{array}{l}(3)CH_2C_6H_5\\(4)ONa\\(6)\end{array}\right. \;>O \\ C=(1)C_6H_3\left\{\begin{array}{l}(6)\\(4):O\end{array}\right. \\ \diagdown(1)C_6H_4(2)CO_2Na\end{array}$	....
Coerulein. Alizarine Green. Anthracene Green.	$\begin{array}{l} \quad (1)C_6H_3\left\{\begin{array}{l}(4):O\\(5)OH\\(6)\end{array}\right. \;>O \\ C—C_6H\left\{\begin{array}{l}(6)\\(5)OH\\(4)OH\\(2)CO\end{array}\right. \\ \diagdown(1)C_6H_4(2)—\mid\end{array}$	From gallein by action of sulphuric acid.
Coerulein S, SW.	Sodium bisulphite compound of coerulein.	....
Cotton Rhodine BS.	$\left[\begin{array}{l} \quad (1)C_6H_2\left\{\begin{array}{l}(5).CH_3\\(4)=NH——\\(2)\end{array}\right. \;>O \\ C=(1)C_6H_3\left\{\begin{array}{l}(2)\\(4):N(CH_3)_2Cl\end{array}\right. \\ \diagdown(1)C_6H_4(2)COOC_2H_5\end{array}\right]_2 CH_2$	Action of formaldehyde on ethyl ester of trimethyl-rhodamine.
Cyanosin. Methyl Phloxin.	$\begin{array}{l} \quad (1)C_6HBr_2\left\{\begin{array}{l}(4)OK\\(6)\end{array}\right. \;>O \\ C=(1)C_6HBr_2\left\{\begin{array}{l}(6)\\(4)=O\end{array}\right. \\ \diagdown(1)C_6H_2Cl_2.COOCH_3\end{array}$	Alkylation of phloxin.
Cyclamin.	$? \; \begin{array}{l} \quad C_6HBr_2\left\{\begin{array}{l}OK\end{array}\right. \;>S \\ C=C_6HBr_2\left\{\begin{array}{l}:O\end{array}\right. \\ \diagdown C_6H_2Cl_2.CO_2K.\end{array}$	From dichloro-fluorescein and sodium sulphide and subsequent bromination.
Eosin, A, Yellowish, G extra, GCF, 3J, 4J, etc., etc.	$\begin{array}{l} \quad (1)C_6H\left\{\begin{array}{l}(3)Br\\(4)ONa\\(5)Br\\(6)\end{array}\right. \;>O \\ C=(1)C_6H\left\{\begin{array}{l}(6)\\(5)Br\\(4):O\\(3)Br\end{array}\right. \\ \diagdown(1)C_6H_4(2)CO_2Na\end{array}$	By bromination of fluorescein.
Eosin BN Safrosin Eosin Scarlet B., etc., etc.	$\begin{array}{l} \quad (1)C_6H\left\{\begin{array}{l}(3)NO_2\\(4)OK\\(5)Br\\(6)\end{array}\right. \;>O \\ C=(1)C_6H\left\{\begin{array}{l}(6)\\(5)Br\\(4):O\\(3)NO_2\end{array}\right. \\ \diagdown(1)C_6H_4(2)CO_2K.\end{array}$	Nitration of dibromo-fluorescein.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown powder, red solution with yellow fluorescence.	Red ppt.	Orange.	Yellow solution. Green fluorescence.	Red.	Dyed on a tannin mordant.
Brown powder, brown solution, green fluorescence.	Darker.	Yellow ppt.	Yellow	Yellow ppt.	
Black paste. Insoluble.	Green.	No change.	Brown.	Black ppt.	
Black powder, brown solution.	Green ppt.	No change.	Brown.	Black ppt.	
Red-brown powder, bluish-red solution.	Scarlet ppt.	Reddish-brown ppt.	Yellow brown solution.	Reddish-brown ppt.	Dyes cotton tannined a bright violet red.
Red powder.	No change (alcoholic solution).	Fluorescence disappears (alcoholic solution).	Yellow.	Brown ppt.	Soluble in alcohol with yellow fluorescence.
Brown powder, red solution.	No change.	Precipitate.	Orange.		
Bluish-red crystals, red solution, green fluorescence.	No change.	Orange ppt.	Yellow.	Orange ppt.	Soluble in alcohol with green fluorescence.
Brown crystalline powder, orange solution.	No change.	Ppt.	Brown solution.	Ppt.	

Commercial name	Formula	Remarks
Erythrin Methyl Eosin. Spirit Eosin Primerose à l'alcool, DH.	$C_6HBr_2 \{ OK$ $>O$ $C \; C_6HBr_2 \{ :O$ $C_6H_4.COOCH_3$	Alkylation of eosin.
Erythrosin, D, B. Pyrosin B. Iodeosin B. Eosin bluish. Eosin J.	$C_6HI_2 \{ ONa$ $>O$ $C{=}C_6HI_2 \{ :O$ $C_6H_4.CO_2Na.$	....
Erythrosin G. Dianthin G. Pyrosin J. Iodeosin G.	$C_6H_2I \{ OK$ $>O$ $C{=}C_6H_2I \{ :O$ $C_6H_4.CO_2K$	....
Ethyl Eosin Rose JB.	$C_6HBr_2 \{ OK$ $>O$ $C{=}C_6HBr_2 \{ :O$ $C_6H_4.COOC_2H_5$	Alkylation of eosin.
Fluorescein Uranin.	$(1)C_6H_3 \{ (4)ONa$ $(6) >O$ $C{=}(1)C_6H_3 \{ (6)$ $(4):O$ $(1)C_6H_4(2)CO_2Na$	Condensation of phthalic anhydride with resorcinol.
Gallein. Alizarine Violet. Anthracene Violet.	$(1)C_6H_2 \{ (4)OH$ $(5)OH$ $(6) >O$ $C-(1)C_6H_2 \{ (6)$ $(5)OH$ $(4)OH$ $(1)C_6H_4(2).CO.O$	From gallic acid and phthalic anhydride.
Irisamine G. Rhodine 3G.	$(1)C_6H_2 \{ (5)CH_3$ $(4)NH_2$ $(2) >O$ $C{=}(1)C_6H_3 \{ (2)$ $(4):N(CH_3)_2Cl$ $(1)C_6H_4(2)COOC_2H_5$	....
Phloxin. Phloxin P. New Pink.	$C_6HBr_2 \{ OK$ $>O$ $C{=}C_6HBr_2 \{ :O$ $C_6H_2Cl_2.CO_2K$	From dichlorophthalic anhydride and resorcinol with subsequent bromination.

Character of dysetuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Green powder, red solution in hot water.	Darker.	Yellow ppt.	Yellow.	Brownish-yellow ppt.	Soluble in alcohol. The corresponding ethyl ester is known as Eosin S, BB. Rose JB à l'alcool, Primerose à l'alcool, etc.
Brown powder, red solution, non-fluorescent.	No change.	Yellow ppt.	Yellow.	Yellow ppt.	
Brown powder, red solution, non-fluorescent.	No change.	Yellow ppt.	Yellow.	Yellow ppt.	
Brown powder, red solution, slight fluorescence.	Yellow ppt.	Brown ppt.	Yellow.		
Brown powder, yellow solution, strong green fluorescence.	Darker.	Yellow ppt.	Yellow solution. Green fluorescence.	Yellow ppt.	Soluble in alcohol.
Violet paste or green powder, red solution.	Blue.	Brown.	Orange.	....	Soluble in alcohol.
Green crystalline powder, carmine red solution.	Scarlet ppt.	Yellow colour restored on dilution.	Yellow solution.	Colour restored.	Unaltered by stannous chloride in hydrochloric acid.
Yellow powder, red solution, green fluorescence.	Bluer.	Yellow ppt.	Yellow.	Brown ppt.	

Commercial name	Formula	Remarks
Phloxin TA. Phloxin. Eosin 10B. Erythrosin B.	$C\left\{\begin{array}{l} C_6HBr_2\left\{ONa\right. \\ \qquad >O \\ =C_6HBr_2\left\{:O\right. \\ C_6Cl_4.CO_2Na \end{array}\right.$	From tetrachlorophthalic acid.
Pyronin B.	$C\left\{\begin{array}{l} =(1)C_6H_3\left\{(4):N(C_2H_5)_2Cl\right. \\ \qquad (6)(6)>O \\ (1)C_6H_3\left\{(4)N(C_2H_5)_2\right. \end{array}\right.$	Resembles pyronine G.
Pyronine G. Casan Pink.	$C\left\{\begin{array}{l} =C_6H_3\left\{:N(CH_3)_2Cl\right. \\ \qquad >O \\ C_6H_3\left\{.N(CH_3)_2\right. \end{array}\right.$	Form formaldehyde and dimethyl-*m*-aminophenol.
Rhodamine B or O Safraniline.	$C\left\{\begin{array}{l} (1)C_6H_3\left\{(4)N(C_2H_5)_2\right. \\ \qquad (6)(6)>O \\ =(1)C_6H_3\left\{(4):N(C_2H_5)_2Cl\right. \\ (1)C_6H_4(2)CO_2H \end{array}\right.$	From phthalic anhydride and dimethyl-*m*-aminophenol.
Rhodamine 3B. Anisoline.	$C\left\{\begin{array}{l} C_6H_3\left\{N(C_2H_5)_2\right. \\ \qquad >O \\ =C_6H_3\left\{:N(C_2H_5)_2Cl\right. \\ C_6H_4.COOC_2H_5 \end{array}\right.$	By esterification of rhodamine B.
Rhodamine G and G extra.	$C\left\{\begin{array}{l} (1)C_6H_3\left\{(4)NHC_2H_5\right. \\ \qquad (2)(2)>O \\ =(1)C_6H_3\left\{(4):N(CH_3)_2Cl\right. \\ (1)C_6H_4(4)COOH \end{array}\right.$	....
Rhodamine 6 G. Trianisoline.	$C\left\{\begin{array}{l} C_6H_3\left\{NHC_2H_5\right. \\ \qquad >O \\ =C_6H_3\left\{:NH(C_2H_5)Cl\right. \\ C_6H_4.COOC_2H_5 \end{array}\right.$	....
Rhodamine 12 GM.	$C\left\{\begin{array}{l} (1)C_6H_3\left\{(4)OCH_3\right. \\ \qquad (2)(2)>O \\ =(1)C_6H_3\left\{(4)N(CH_3)_2Cl\right. \\ (1)C_6H_4(2)COOC_2H_5 \end{array}\right.$	From dimethylamino-hydroxybenzoyl benzoic acid and methyl resorcin. Subsequently esterified.
Rhodamine S.	$C\left\{\begin{array}{l} C_6H_3\left\{N(CH_3)_2\right. \\ \qquad >C \\ =C_6H_3\left\{N(CH_3)_2Cl\right. \\ CH_2.CH_2.COOH \end{array}\right.$	From succinic anhydride and dimethyl-*m*-aminophenol.
Rhodine 2G	$C\left\{\begin{array}{l} (1)C_6H_3\left\{(4)NH.C_2H_5\right. \\ \qquad (2)(2)>O \\ =(1)C_6H_3\left\{(4):N(CH_3)_2Cl\right. \\ (1)C_6H_4.(4)COOC_2H_5 \end{array}\right.$	....

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Red powder, bluish-red solution, green flourescence.	No change.	Red ppt.	Yellow.	Orange ppt.	
Fluorescence has a somewhat redder shade than that of Pyronine G.	....	....	....	....	Dyes cotton mordanted with tannic acid a bluish-red.
Green crystal, red solution, yellow flourescence.	Pale red ppt.	Bright orange in excess.	Orange.	Red.	As pyronine B.
Green crystals, bluish-red solution, strong fluorescence.	Red ppt.	Green ppt. soluble in excess.	Brownish-yellow.	Bluish-red.	Soluble in alcohol. With stannous chloride in hydrochloric acid goes brighter.
Red powder, red solution with fluorescence.	Red ppt. on heating.	Yellow.	Yellow.	Red.	Soluble in alcohol. With stannous chloride in hydrochloric acid; scarlet.
Orange powder, violet solution with fluorescence.	Solution decolourised on heating with precipitation of base.	Yellow.	Yellow.	Red fluorescent solution.	Soluble in alcohol.
Brown powder, red solution (pink) green flourescence.	Light red. ppt.	Yellow. Pink on dilution.	Yellow.	Pink.	Soluble in alcohol. Goes to a brighter shade with stannous chloride and hydrochloric acid.
Red-brown powder, yellow-red solution.	Bright red ppt.	No change.	Yellow solution.	Orange.	Dyes silk and tannined cotton yellowish red.
Crystalline powder, red solution with yellow fluorescence.	Decolourised	Orange. Yellow. Pink on dilution.	Yellow.	Pink.	Brighter with stannous chloride in hydrochloric acid. Orange-red with nitric acid (S. G. 1.40).
Green crystalline powder, carmine red solution.	Scarlet ppt.	No change.			Soluble in alcohol with scarlet colour and green fluorescence.

Commercial name	Formula	Remarks
Rhodine 12 GF.	$(1)C_6H_3$ { $(4)OH$, (2) >O } CH_2 $C=(1)C_6H_3$ { (2), $(4):N(CH_3)_2Cl$ } $(1)C_6H_4(2)COOC_2H_5$ — 2	By action of formaldehyde. ? Constitution.
Rosamine.	$C_6H_5.C$ C_6H_3 { $:N(CH_3)_2Cl$, >O } C_6H_3 { $N(CH_3)_2$ }	From benzotrichloride and dimethyl-*m*-aminophenol.
Rose Bengale.	C_6HI_2 { OK, >O } $C=C_6HI_2$ { :O } $C_6H_2Cl_2.COOK.$	Action of iodine on dichlorofluorescein
Rose Bengale, B, 3B.	C_6HI_2 { OK, >O } $C=C_6HI_2$ { :O } $C_6Cl_4.CO_2K.$	From tetra-chlorofluorescein.
Safrosin.	$C_6H(NO_2)Br$ { OK, >O } $C=C_6H(NO_2)Br$ { :O } $C_6H_4.CO_2K$	Nitration of dibromo fluorescein.
Violamine B. Fast Acid Violet B.	$(1)C_6H_3$ { $(4)NH.C_6H_4.SO_3Na$, (6) >O } $C=(1)C_6H_3$ { (6), $(4):NHC_6H_5$ } $(1)\ C_6H_4(2).CO.O$	From fluorescein chloride, *i. e.*, dichlorofluoran $C_{20}H_{10}O_3Cl_2$.
Violamine 3B. Fast Acid Blue R.	$(1)C_6H_3$ { $(4).NH.C_6H_4$ { OC_2H_5, SO_3Na. }, (2) >O } $C=(1)C_6H_3$ { (2), $(4):NH(C_6H_4OC_2H_5)$ } $(1)C_6H_2$ { $(1).CO.O$, $(4)Cl$, $(5)Cl$ }	From *p*-phenetidine and dichloro fluorescein chloride subsequent sulphonation.
Violamine G. Acid Rosamine A.	C_6H_3 { $NH.C_6H_2$ { $(CH_3)_3$, SO_3Na }, >O } $C=C_6H_3$ { $:NH.C_6H_2(CH_3)_3$ } $C_6H_4.CO—O$	Action of mesitylene on fluorescein chloride and subsequent sulphonation.
Violamine R. Fast Acid Violet A2R Acid Violet 4R.	C_6H_3 { $NH.C_6H_3$ { CH_3, SO_3Na }, >O } $C=C_6H_3$ { $:NH.C_6H_4.CH_3$ } $C_6H_4.CO-O$	....
Violamine 2R.	C_6H_3 { $NH.C_6H_3$ { OC_2H_5, SO_3Na }, >O } $C=C_6H_3$ { $:NH.C_6H_4.OC_2H_5$ } $C_6H_2Cl_2.CO.O$	....

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Bright red powder, yellow-red solution.	Bright red ppt.	No change.	Yellow.	Orange.	Used for cotton and silk printing.
Bluish-red solutions with yellow fluorescence.	Decolourised. Ppt.	Orange-red.	Orange-red.	Bluish-red.	Have not attained technical importance.
Brown powder, red solution, no fluorescence.	No change.	Red ppt.	Yellow.	Red ppt.	
Red powder, bluish-red solution.	No change.	Pink ppt.	Brown.	Pink ppt.	
Brown crystals, orange solution.	No change.	Ppt.	Yellow.	Ppt.	
Violet powder, violet solution.	No change.	Blue ppt.	Orange.	Blue ppt.	Nitric acid (sp.gr. 1.40); scarlet.
Dark violet powder, dark blue solution.	Violet. Redder on heating.	Blue flocculent ppt.	Bordeaux coloured solution.	Reddish violet, eventually ppt.	
Red powder, red solution.	Yellow.	Red ppt.	Yellow.	Red ppt.	
Red powder, red solution.	No change.	Violet ppt.	Dull red.	Violet ppt.	Goes bluer with stannous chloride in hydrochloric acid.
Violet powder, blue solution.	Violet.	Blue ppt.	Red.	Blue ppt.	

8. INDAMINES AND INDOPHENOLS.

By the simultaneous oxidation of 1 molecule of a monamine with 1 of a *p*-diamine containing at least 1 primary amino-group, substances are produced known as indamines. The simplest indamine resulting from the oxidation of a mixture of *p*-phenylenediamine and aniline must, as free base, possess the constitution

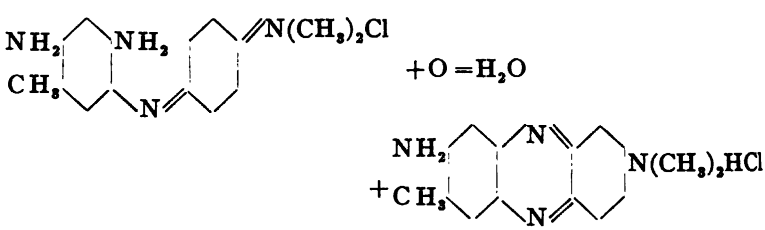
$$NH_2.C_6H_4.N:C_6H_4:NH.$$

Its salts are greenish-blue and soluble in water, it is unstable toward an excess of acid, yielding quinone, and on heating with an aqueous solution of an aniline salt, phenosafranine is produced.

The indamine obtained by the oxidation of dimethyl-*p*-phenylenediamine and dimethylaniline, known only as quinonoid ammonium salts under the name of *Bindschedler's Green* has no technical importance, being easily decomposed by excess of acids and alkalies.

The simplest indamine yields *p*-diamino-diphenylamine on reduction; Bindschedler's Green gives the corresponding tetramethyl derivative.

Tolylene Blue (*Toluylene Blue*) is more stable and may be obtained by the action of the hydrochloride of nitrosodimethylaniline on *m*-tolylene-diamine or by the simultaneous oxidation of the latter base with dimethyl-*p*-phenylenediamine. Its constitution and conversion into the azine dyestuff, *Tolylene Red* on heating are represented by the equation:



The **indophenols** differ from the indamines in that they are used technically. The chief member of the class is prepared by reducing nitrosodimethyl-aniline in aqueous solution to dimethyl-paraphenyl-

enediamine, $NH_2.C_6H_4.N(CH_3)_2$, filtering and treating the filtrate with a solution of 2 molecules of α-naphthol in sodium hydroxide. Potassium dichromate is next added, and then acetic acid till the liquid acquires an acid reaction, when the colouring matter is precipitated. Indophenol may also be obtained by the direct action of nitrosodimethylaniline on α-naphthol.

Indophenol or Naphthol Blue, $C_{18}H_{16}N_2O$, prepared as above, is a feeble base which probably has the constitution expressed by the formula: $(CH_3)_2N.C_6H_4.N:(1)C_{10}H_6(4):O$.

This is borne out by its reduction by stannous acetate to a leuco-compound possessing both acid and basic properties, and having the formula: $(CH_3)_2N.C_6H_4.NH.C_{10}H_6.OH$.

Commercial *Indophenol N* forms a blue paste or dark brown powder, which when dry has a coppery reflection and closely resembles some varieties of indigo. When heated it sublimes in needles. Indophenol is quite insoluble in water, but dissolves in alcohol with a blue colour, and in strong sulphuric acid with a dirty yellow-brown colour, the solution giving a brown precipitate on dilution. The alcoholic solution is turned reddish-brown by hydrochloric acid, but is unchanged by alkalies. The alkaline solution, or the solid dye in presence of alkali, is decolourised by reducing agents, such as stannous chloride or glucose, so that a vat can be prepared from indophenol in the same way as from indigo.

Reduced indophenol, or **white indophenol,** $C_{18}H_{18}N_2O$, occurs in commerce as a yellowish-white paste, soluble in pure or acidified water. It is not changed by hydrochloric acid. In presence of an alkali and air it gradually oxidises to blue indophenol, or immediately on cautious treatment with potassium dichromate or a hypochlorite.

Indophenol is employed as a substitute for indigo in wool and cotton dyeing. It forms a lake with chromic oxide. On the fibre it is best recognized by being turned greyish-brown or dark grey by treatment with somewhat dilute (10%) hydrochloric acid, while indigo and other dark blue dyes are unaffected.

Indophenol may be applied as an ingrain colour by impregnating the material with a mixture of the diamine and phenol, and subsequently developing the colour by oxidation with potassium dichromate or bleaching powder. The colours obtained with indophenol are very fast to soap and light, but being very sensitive toward acids, prevents the substitution of indophenol for indigo.

Aniline Black.—By the oxidation of aniline under suitable conditions a very stable black colouring-matter is formed. The most perfect black is yielded by pure aniline boiling at 182°.

Although the constitution of aniline black cannot be safely regarded as quite settled, Willstätter's recent work points to its being a complicated indamine and for that reason it will be considered under the same heading as indamines and indophenols.

The oxidation of aniline to aniline black may be effected by potassium dichromate, permanganate, or chlorate, and by various other oxidising agents. In practice, a readily changeable metallic salt is employed as a carrier of oxygen, a very suitable combination being a chlorate (preferably that of sodium) and cupric sulphate. Ammonium vanadate now receives an application in the production of aniline black, as it is readily reduced to vanadium chloride, and this is immediately reoxidised to a vanadate by the chlorate simultaneously employed. 1 part of vanadium will do the work of 4,000 of copper, and suffice for the production of from 10,000 to 20,000 parts of aniline black. Electrolytic oxygen may also be employed for producing aniline black.

To produce aniline black in a pure state, 40 parts of aniline hydrochloride, 40 of cupric sulphate, 20 of potassium chlorate, and 16 parts of ammonium chloride should be dissolved in 500 parts of water, and the solution heated to about 60°. The black precipitate formed may be purified, if desired, by boiling it successively with hydrochloric acid, alcohol, ether, benzene, and chloroform. The product is the hydrochloride of a base called nigraniline, which may be obtained in a free state by treating the colouring matter with a dilute alkali.

Nigraniline has often been regarded as having the empirical formula C_6H_5N; its molecular formula was regarded by Nietzki as $C_{30}H_{25}N_5$. According to Liechti and Suida, however, aniline black is a chlorinated base called emeraldine, containing $C_{18}H_{14}ClN_3$, all the salts of which contain chlorine, which cannot be removed even by treatment with argentic oxide. Aniline black is turned dark green by sulphurous acid, and other mineral acids also affect it; but if it be treated with an acid solution of potassium dichromate the black colour becomes permanent, and is no longer affected by treatment with acids or reducing agents. According to Liechti and Suida, this unalterable black is not a chromate of the base, but the compound of an oxidation-product with chromic oxide (Cr_2O_3).

By treatment with tin and hydrochloric acid, aniline black is reduced to paradiaminobenzene, paradiamino-diphenylamine, and other products.

Powerful oxidising agents, such as chromic acid mixture, convert aniline black into quinone, $C_6H_4O_2$.

Aniline black dissolves in strong sulphuric acid to form sulphonic acids, which are insoluble in acidified water, and are, therefore, precipitated on adding water to the solution. On protracted washing with water the precipitate dissolves with green colour. The alkali-metal compounds of sulphonated aniline black dissolve in water with blue-black colour. The solutions are decolourised by reducing agents (*e. g.*, zinc-powder, glucose), but recover their original tint on exposure to air. The fact is employed for the preparation of an aniline-black vat.

Aniline black differs remarkably from most other aniline colours in that it is wholly insoluble in water, alcohol, acids, soap-lye, and alkaline solutions. Hence the application of ready-formed aniline black is very limited, and it is usually produced in the fibre itself. It yields an extremely fast and pure black on cotton, but it is not well suited for dyeing silk or wool. Its chief application is in the dyeing of cotton hosiery where its great fastness and permanence render it an especially desirable dye. Many precautions, however, must be employed in the proper dyeing of it, as it is a process which is very liable to tender the fibre, owing to the acid fumes liberated in the oxidation of the dyestuff.

On the fibre, aniline-black is easily recognised by its resistance to reagents,[1] being unchanged by alkalies, and either wholly unchanged by acids or turned slightly greenish, the black colour being restored by alkalies. Weak oxidising agents have no effect, but if the fibre be treated alternately with strong solutions of potassium permanganate and oxalic acid, several times in succession, the colour will be destroyed. Hypochlorites change the colour to brownish-red, but if the fibre thus treated be washed and exposed to the air, it slowly becomes black again. The constitution of aniline black has recently aroused considerable interest and A. G. Green (VII *International Congress of Applied Chemistry*, London, 1909; *J. Soc. Dyers*, 1909, **25**, 188) proposed the

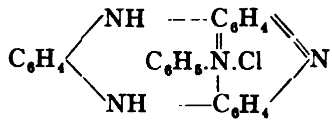
[1] Fibres dyed with *logwood black* leave on ignition an ash containing iron or chromium as also do *madder* and *tannin blacks*. These blacks are reddened by dilute hydrochloric acid, and are readily bleached by bromine water or hypochlorites.

Commercial name	Formula	Remarks
Aniline Black in paste.	$C_6H_5.N:C_6H_4:N.C_6H_4.N:C_6H_4:N.C_6H_4.N:C_6H_4:$- $N.C_6H_4.N:C_6H_4:NH$ (?)	By oxidation of aniline, usually in presence of a catalytic agent.
Clayton Fast Blacks. Clayton Fast Greys.	....	By action of nitrosophenol, etc. on thiosulphuric acid in acid solution.
Durophenine Brown.	....	By heating nitrosophenol with dilute sulphuric acid.
Indochromogen S.	$C_6H_3\begin{cases}(1).N(1)C_{10}H_4\begin{cases}(3)OH\\(4):O\\(7)SO_3Na.\end{cases}\\(2)S.SO_2Na\\(4)N(C_2H_5)_2)\end{cases}$	From 1:2-Naphtha-quinone-4:6-disulphonic acid and diethyl-*p*-phenylene-diamine thiosulphonic acid.
Indophenol.	$(CH_3)_2N(1).C_6H_4(4).N:(1)C_{10}H_6(4):O$	Oxidation of dimethyl-*p*-phenylene diamine with *a*-naphthol.
Indophenol white (Leucoindophenol.)	$(CH_3)_2N(1).C_6H_4(4).NH.(1)C_{10}H_6(4).OH$	By reduction of indophenol.
New Grey. Nigrisine. Methylene Grey. NewMethylene Grey. Direct Grey, etc.	....	By boiling solution of nitroso-dimethyl-aniline hydrochloride.
Ursol D, P, DD.	....	Produced on fibre by oxidation of *p*-phenylene-diamine

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Paste, but generally developed on the fibre.	....	....	Black solution.	Greenish-black.	By stannous chloride in hydrochloric acid; greener.
Black powder. Insoluble in water, easily soluble in sodium sulphide.	No ppt.	Black ppt.	Black solution.	Black ppt.	Dye cotton grey or black from a sodium sulphide bath.
Black powder. Soluble in alkalies and alkaline sulphides. Insoluble in water.	No ppt.	Blackish-brown ppt.	Violet-black solution.	Dark brown ppt.	Dyes cotton deep brown from a sodium sulphide bath.
Blue powder, reddish-violet solution.	Dirty violet. Blue on boiling.	Yellowish-brown.	Greenish-yellow.	Yellowish-brown.	The blue colour on boiling is due to the formation of Indochromine T (Brilliant Alizarine Blue G, R). Indochromogen is printed with chrome mordant and steamed.
Blue paste or dark brown powder with coppery lustre. Insoluble in water.	Insoluble in aqueous alkalies. Alcoholic solution unchanged.	Alcoholic solution turned reddish-brown.	Yellow-brown solution.	Brown ppt.	Sublimes in needles on heating. On fibre hydrochloric acid (10%) gives greyish-brown or dark grey. (Indigo in unaffected.)
Yellowish-white paste.	Alkaline solution oxidised on exposure to air. Indophenol precipitated.	Unchanged.			
Greyish-black powder, reddish-grey solution.	Grey-black ppt. of base.	Grey-blue.	Greenish.	Reddish-grey.	

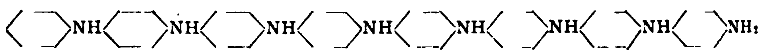
following constitutional formulæ for the stages in the formation of aniline black:

Emeraldine ($C_{18}H_{18}N_3$) Nigraniline ($C_{18}H_{12}N_3Cl$)



Ungreenable black.
($C_{24}H_{19}N_4Cl$)

R Willstätter (*Ber.*, 1909, **42**, 2147, 4118) states that aniline black is derived from a leuco-base, $C_{48}H_{42}N_8$ or constitutionally



By oxidation either 3 or 4 of the benzene nuclei can become quinonoid, the last stage of the oxidation being

$$C_6H_5.N{:}C_6H_4{:}N.C_6H_4.N{:}C_6H_4{:}N.C_6H_4.N{:}C_6H_4{:}N.C_6H_4.N{:}C_6H_4{:}NH$$

In either case the :NH group may be hydrolysed and replaced by :O; for the reactions of these different forms of aniline black, reference may be made to Willstätter and Dorogi (*Loc. cit.*, 4122).

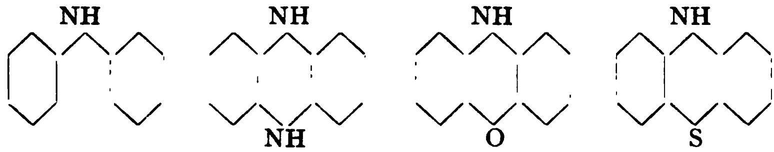
Another view of the constitution of aniline black is due to Bucherer (*Ber.*, 1909, **42**, 2931) who regards it as a composite azine. (See further Green and Woodhead, *Trans.*, 1910, **97**, 2388.)

Indochromogen S is an indophenol produced by the condensation of 1:2-naphthaquinone-4:6-disulphonic acid with diethyl-*p*-phenylene-diamine-thiosulphonic acid which furnishes **Indochromine T**, (*Brilliant Alizarine Blue*) a thiazine dyestuff. Indochromogen S is a blue powder giving a reddish-violet solution; it is printed with a chrome mordant and steamed, whereby the resulting indochromine is fixed on the fibre.

9. AZINE DYESTUFFS.

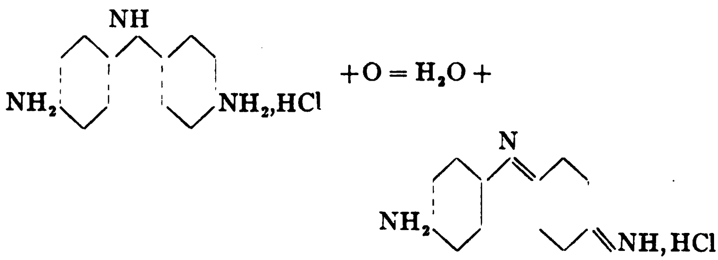
As the pyronine, fluoresceïn and acridine dyestuffs differ from those of the di- and tri-phenylmethane series by the linking up of 2 of the benzene nuclei by a bridge oxygen or nitrogen atom to give a pyrone-

or pyridine-ring, so the introduction of nitrogen, oxygen or sulphur into the indamines and indophenols gives rise to azine, oxazine or thiazine derivatives. Just as leuco-indamines are amino-derivatives of diphenylamine, so the leuco-compounds obtained from azine, oxazine and thiazine dyestuffs may be considered as derived from dihydrophenazine, phenoxazine and thio-diphenylamine respectively. The relationships of these compounds to diphenylamine are rendered evident by the following formulæ:

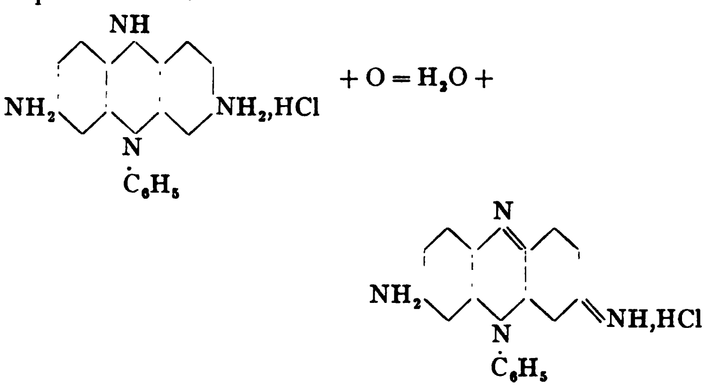


Diphenylamine. Dihydrophenazine. Oxazine. Thiodiphenylamine.

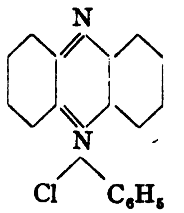
Since the oxidation of a *pp*-diamino-diphenylamine salt can only result in the production of a *p*-quinonoid indamine



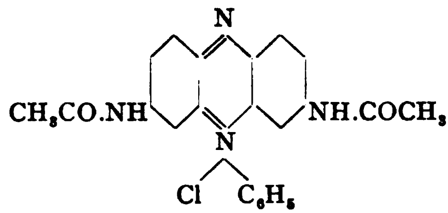
it seems but natural to assign a corresponding quinonoid structure to phenosafranine, representing the oxidation of its leuco-compound by the equation



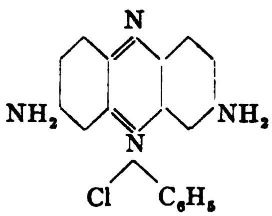
Phenosafranine salts are, however, derived from a powerful base, and quaternary ammonium salts still remain when the amino-groups are acetylated or even removed, so that phenylphenazonium chloride and diacetylsafranine chloride having to be represented by formulæ I and II respectively, the possibility of phenosafranine as chloride possessing structure III must be taken into account.



I. Phenylphenazonium chloride.

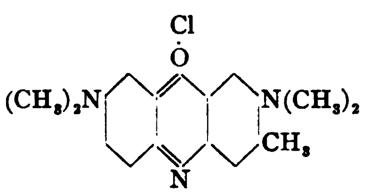


II. Diacetylsafranine.

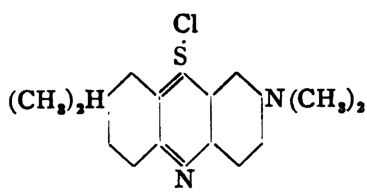


III. Phenosafranine.

A. G. Green (*Pros. Chem. Soc.*, 1892, **8**, 195; 1896, **12**, 226; *Rev. Gén. Mat. Col.*, 1897 **1**, 269) has strongly advocated an ortho-quinonoid formula for the azines, oxazines and thiazines on the ground of the ready reoxidisability of their leuco-compounds. Kehrmann (*Ber.*, 1899, **32**, 2601) also looks on the dyestuffs of these 3 series as being ortho-quinonoid in structure and strictly analogous, formulating Capri Blue and Methylene Blue as oxonium and sulphonium salts respectively.



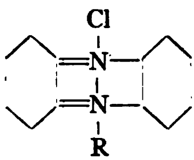
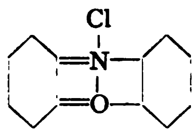
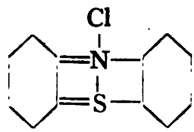
Capri blue.



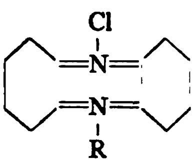
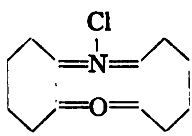
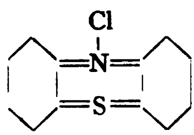
Methylene blue.

Many chemists, however, still regard these substances as possessing a paraquinonoid structure and as ammonium salts. (See especially Hantzsch, *Ber.*, 1905, **38**, 2146; 1906, **39**, 153, 1365.)

Green (*Ber.*, 1899, **32**, 3155) while in favour of similar ortho-quinonoid formulæ for the 3 classes of dyestuffs represents them as ammonium salts in one or other of the following ways:

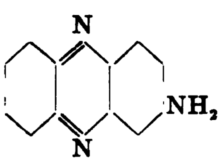
or or

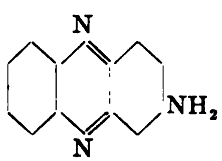




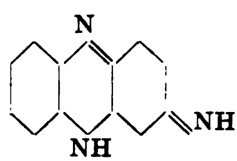
Azine. Oxasine. Thiazine.

In the description given of the different dyestuffs, formulæ will be employed according to convenience and without prejudice; the same remarks apply to the oxazine and thiazine series.

The dyestuffs containing azine rings may be divided into 2 classes according to whether the nitrogen atoms of the ring are united to alkyl or aryl groups or merely to hydrogen. The *eurhodines* in which these alphyl groups are wanting, are far weaker bases, their salts being readily hydrolysed; while in the case of aposafranine one encounters the salts of a powerful base. The simplest eurhodine can be written with either of the tautomeric formulæ (I, II or III):

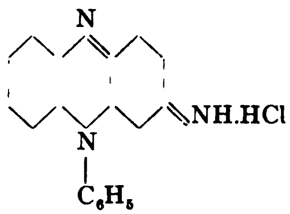

I


II

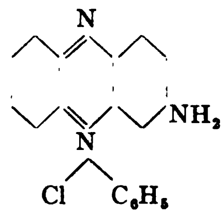

III

Now aposafranine chloride (the product obtained from pheno-

safranine by the elimination of an amino-group) must be either (IV or V)

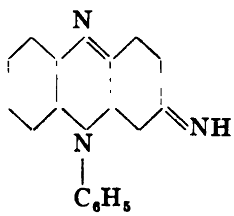


IV

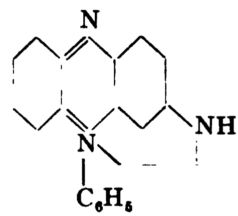


V

and if a free anhydro base could be obtained from it, it would have to be written either as VI or VII:



VI



VII

The marked increase in basicity occasioned by replacing a hydrogen atom by phenyl certainly points to the free base of the simplest eurhodine being aminophenazine and aposafranine as a quarternary salt of amino-phenyl-phenazonium.

Eurhodines.—The eurhodines are usually prepared technically by the condensation of nitrosodimethylaniline hydrochloride with *m*-diamines, the indamine so obtained passing into an azine on warming with simultaneous oxidation.[1] Eurhodines are also obtained by the action of monamines on *o*-amino-azo-compounds at 140° (Otto N. Witt) and by the condensation of quinone-dichloro-diimide with primary bases.

Neutral Violet, $C_{14}H_{14}N_4,HCl$, is produced by the action of nitroso-dimethylaniline on *m*-phenylenediamine. The commercial colouring matter is a greenish-black powder, the dust of which is intensely irritating to the mucous membrane. It dissolves easily in

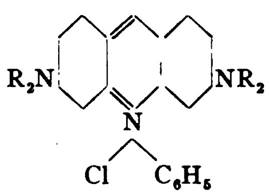
[1] See under Tolylene Blue for its conversion to Tolylene Red.

water with violet-red colour. The solution is scarcely changed by a little hydrochloric acid, but is turned blue by excess. Sodium hydroxide produces a brown precipitate. In concentrated sulphuric acid the dye dissolves with a green (or, according to Zetter, a dirty violet) colour, which on adding water becomes blue, and on further dilution violet.

Neutral Red or Tolylene Red, $C_{15}H_{16}N_4$,HCl, is homologous with the last colour. It forms a greenish-black powder easily soluble in water with a bluish-red colour, which turns bluer and then disappears on warming with zinc and hydrochloric acid, but returns on exposing the reduced solution to the air. In alcohol the dye dissolves to a magenta-red solution, which exhibits a strong brownish-red fluorescence. With hydrochloric acid the aqueous solution becomes bluer, and with excess, pure blue. With sodium hydroxide it yields a yellowish-brown precipitate, soluble in ether with greenish-yellow fluorescence. In strong sulphuric acid, tolylene red dissolves with a bluish-green colour, changing to blue and magenta-red on adding water.

The eurhodols in which the amino-groups of the eurhodines are replaced by hydroxyl are of no particular interest from a technical point of view; they exhibit tautomerism giving a mixture of N- and O-alkyl ethers on alkylation. (Kehrmann and Messinger, *Ber.*, 1891, 24, 2167.)

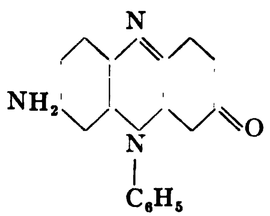
Safranines.—Considerable confusion has arisen as to the relationships existing between the group of dyestuffs known as safranines and the large group of indulines, substances produced by heating azo-compounds with primary bases. It will probably be as well to restrict the name of safranines to compounds such as



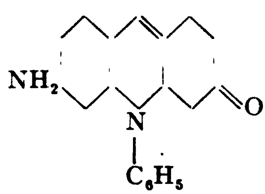
(R=H or alkyl.)

its homologues and analogous compounds in which 1 or more benzene nuclei may be replaced by naphthalene, etc. The safranines are generally met with as red monacid salts; dissolved in concentrated sulphuric acid green solutions of triacid salts are produced; addition

of water to the green solution changes the colour to blue (diacid salt) and ultimately red (monacid salt), the monacid salts being remarkably stable. Addition of potassium hydroxide to a cold solution of phenosafranine gives a brown precipitate, but if this be filtered off and washed with cold water it passes once more into solution with the original phenosafranine colour. Heated in sealed tubes with sodium acetate solution, safraninone is produced, while several days boiling with alcoholic potassium hydroxide gives *hydroxyaposafranone*.



Safraninone.



Hydroxyaposafranone.

Since the hydroxyaposafranone produced in this way is identical with the compound obtained by Jaubert through condensing *p*-nitrosophenol with *m*-hydroxydiphenylamine (*Ber.*, 1895, **28**, 273) no doubt can exist as to the symmetry of the 2 amino-groups in phenosafranine. (Hewitt, Newman, Winmill, *Trans. Chem. Soc.*, 1909, **95**, 577.)

The safranines may be obtained:

(a) By heating indamines with primary monamines, a portion of the indamine being simultaneously reduced.

(b) By oxidising a mixture of *pp*-diaminodiphenylamine (or a derivative) with a primary base.

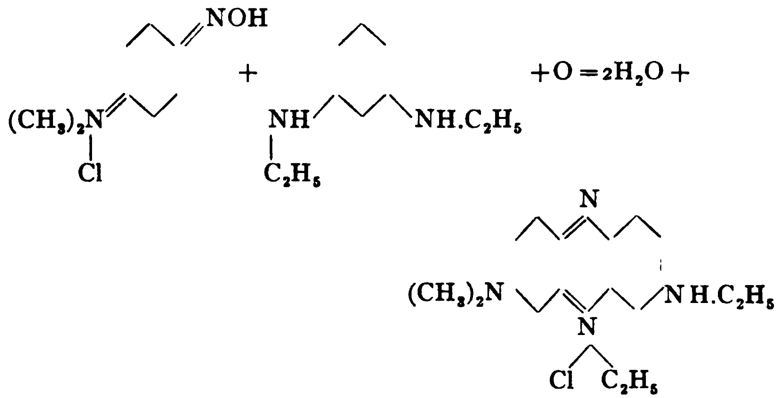
(c) By oxidation of a *p*-diamine with 1 primary amino-group, with 2 molecules of monamine. Two different monamines may be employed, but it is necessary that one, which need not be primary, should have the position para to the amino-group free, while the other, which need not have a free para position, must be primary.

(d) By oxidising a mixture of *m*-amino-diphenylamine or its analogues with *p*-diamines.

Method (c) is most generally employed technically (preparation of safranine, fuchsia, etc.), though for the preparation of individual compounds in a state of purity, methods (a) and (b) have advantages.

A modification of method (d) is to allow the hydrochloride of a nitroso-dialkylaniline to react with a substituted diamine; this gives the

possibility of preparing mixed aliphatic-aromatic safranines in which the phenyl of the azonium group is replaced by an aliphatic radical. As an instance of this reaction Cassella's *Fast Neutral Violet B* may be mentioned; it is prepared with the aid of *sym*-diethyl-*m*-phenylene-diamine.



Safranine, *Safranine T, Safranine extra G,*[1] or *Aniline Pink.* This colouring matter, as it occurs in commerce, is a mixture of several homologous substances, of which $C_{19}H_{17}N_4Cl$, $C_{20}H_{19}N_4Cl$, and $C_{21}H_{21}N_4Cl$ are the chief. Safranine can be obtained by various methods, including the oxidation of mauveine, $C_{27}H_{25}N_4Cl$; the treatment of aniline with glacial acetic acid and lead nitrate; and by heating amino-azotoluene with toluidine nitrate. These methods are obsolete, that now employed being usually the oxidation of a mixture of aniline, *o*-tolidine and *p*-tolylene-diamine in molecular proportions. Aniline oil of suitable composition is first converted into the amino-azo-compounds, amino-azobenzene and amino-azotoluene. When reduced with zinc and hydrochloric acid, the first of these splits into aniline and *p*-phenylene-diamine, and the latter into *o*-toluidine and *p*-tolylene-diamine; thus:

$$C_6H_4(CH_3).N_2.C_6H_3(CH_3).NH_2 + 2H_2 = C_6H_4(CH_3).NH_2 + NH_2.\text{-}C_6H_3(CH_3).NH_2.$$

When the action is complete the liquid is diluted, a molecular proportion of toluidine hydrochloride added, and the mixture oxidised by

[1] Also known as: *Safranine S, Safranine GGS, Safranine GOOO, Safranine FF, Safranine AG* and *AGT* extra.

potassium dichromate. The product is boiled with milk of lime, and the liquid filtered, neutralised with hydrochloric acid, and saturated with salt. The precipitate is purified by solution in water, and again salted out.

Commercial safranine usually occurs as a reddish-brown powder, but the pure hydrochloride forms reddish crystals, soluble in water and alcohol. The alcoholic solution exhibits a fine yellowish-red fluorescence. Alkali hydroxides and ammonia change the colour of an aqueous solution of safranine to brownish-red, but no precipitate is produced unless the liquid is concentrated. The base is best prepared by treating a solution of the hydrochloride with argentic oxide, filtering, and evaporating the filtrate to dryness.

Safranine is one of the few colouring matters which are taken up by animal fibres from alkaline solutions. In alkaline or neutral solution safranine also possesses some affinity for cotton, but the colour produced is not fast. The best mordant is tannin and tartar-emetic.

On the fibre, safranine is distinguished by being unchanged by dilute acid, but turned from red to blue-violet by concentrated hydrochloric acid. Ammonia and sodium hydroxide remove the colouring matter without much previous change of tint. The colour is bleached on warming the fibre with hydrochloric acid and stannous chloride. Alcohol strips fibres dyed with safranine, forming a red solution which exhibits a reddish-yellow fluorescence.

In dilute acid solution only one of the amino-groups of safranine is diazotisable, but both may be diazotised in strong sulphuric acid. By the combination of the monazo-compound with β-naphthol, a blue dyestuff (known as *Indoin*, etc.) is produced which is used in dyeing cotton mordanted with tannin.

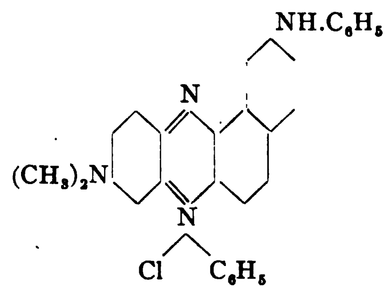
Mauveine, $C_{27}H_{24}N_4$, is of interest as being the base of *Perkin's purple*, *Aniline Violet*, or *Mauve*, the first commercial dye obtained from aniline. The free base may be obtained from adding alkali hydroxide to a boiling alcoholic solution of the crystallised acetate. It then separates as a black glistening powder, which is almost insoluble in ether or benzene, but in alcohol forms a violet solution, which is turned purple an adding a dilute acid, or even by carbonic acid. Mauveine is a strong base, decomposing ammonium salts and forming a carbonate.

Commercial mauve is usually a sulphate of the base. It is now almost obsolete, but occasionally occurs as a reddish-violet paste,

sparingly soluble in hot water with violet-red colour. The solution is not changed by hydrochloric acid, but yields a bluish-violet precipitate with sodium hydroxide and dyes silk a reddish-violet. In an excess of strong sulphuric acid, mauve dissolves with olive-green colour, changing on adding water to green, sky-blue, and finally to reddish-violet.

Magdala Red, $C_{30}H_{21}N_4Cl+H_2O$, may be taken as the typical safranine of the naphthalene series. It is prepared by heating amino-azonaphthalene with α-naphthylamine in acetic acid solution to 150°. *Magdala Red* is characterised by its very sparing solubility in water, even when hot, and by forming a cherry-red alcoholic solution, which exhibits a fluorescence of a remarkable cinnabar-red colour. This behaviour is simulated only by an alkaline solution of azoresorufin; but that substance differs from Naphthalene Red in the colour it dyes silk, and in yielding a brown precipitate on addition of a strong acid. The fluorescence of a solution of Naphthalene Red is destroyed by ammonia or sodium hydroxide. It seems to be still occasionally used in silk dyeing.

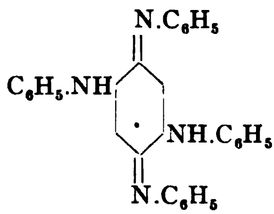
Naphthyl Violet and **Naphthyl Blue** are substituted diamino-derivatives of phenyldinaphthazonium, while *Bâle Blue*, obtained by the condensation of nitroso-dimethylaniline with diphenyl-2:7-naphthylenediamine, has a benzene nucleus on one side and a naphthalene nucleus on the other side of the azine ring. Its constitution is given by



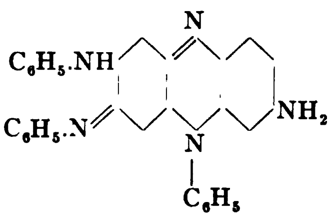
This dye is used on tannin-mordanted goods.

Indulines.—These compounds are very similar to the safranines, being derivatives of phenazine. They are produced by the action of amino-azo-compounds on the hydrochlorides of aromatic amines (*e. g.*, aniline), ammonia being eliminated. The substances of the induline class occurring in commerce are dark-blue or violet dyes, less

remarkable for their brilliancy than their resistance to light and atmospheric influences. Their slighter basicity as compared with the safranines led to misconception as to their structure: while the isolation of oxygen-free bases giving sharp results on analysis seems nearly an impossibility in the case of the safranines, the elements of acid may usually be removed from the indulines with ease. The mechanism of the change by which indulines are produced has only been explained after long researches, one of the most important earlier steps being the recognition by Witt and Thomas (*Trans. Chem. Soc.*, 1883, **43**, 112; *Ber.*, 1887, **20**, 1538) of the intermediate production of azophenine (dianilinoquinonedianil):



a substance whose constitution was recognised by O. Fischer and E. Hepp. From the method of preparing the indulines it is but natural that a mixture of dyestuffs results. Fischer and Hepp (*Zeitsch. f. Farb. Text. Chem.*, 1902, **1**, 457) consider anilinophenosafranine, $C_{24}H_{19}N_5$, as the primitive member of the series. The salts of this base are reddish violet and are fairly soluble in water. The *Induline*, $C_{30}H_{23}N_5$, is obtained heating aminoazobenzene for a short time with aniline hydrochloride or from the hydrochloride of the former base and a large excess of aniline at a higher temperature; it may also be obtained by heating under pressure an alcoholic solution of azophenine, aniline and the hydrochloride of *p*-phenylenediamine. The dystuff gives a hydrochloride which is easily soluble in water, but is precipitated by hydrochloric acid; it is used for cotton printing under the name of "*indamine*" and probably possesses the constitution



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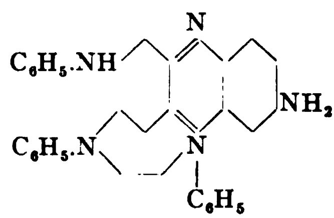


Induline 3 B is according to Fischer and Hepp *phenyl-anilino-mauveine*, $C_{36}H_{27}N_5$, while they look upon *Induline* 6 *B* as its *anilino* derivative $C_{42}H_{32}N_6$.

The characters and reactions of the various commercial indulines are not strictly identical, but do not require separate description. As a class, the indulines usually occur as bluish-black or brownish-black powders, which are insoluble in water but soluble in alcohol with greenish or bluish-violet colour. The alcoholic solution becomes pure blue with hydrochloric acid, and on adding sodium hydroxide yields a dirty-red or reddish-violet solution or precipitate, the exact reaction depending on the nature of dye under examination.

Sulphonated Indulines. Soluble Indulines.—By treating the indulines with strong sulphuric acid, various sulphonated indulines are obtained which are soluble in water. The redder shades are met with in commerce under the name of *Fast Blue R* and *Water-soluble Nigrosine*, and the bluer varieties as *Fast Blue B*, *Fast Blue Greenish*, *Induline* 3 *B* or 6 *B*, etc. These sulphonated indulines occur as crystalline powders with a bronze reflection ("induline"), or as black, glistening fragments ("nigrosine"). They dissolve in water with bluish-violet, and in alcohol with blue colour. Hydrochloric acid renders the solution blue. Alkalies produce a brownish-violet precipitate. In sulphuric acid, the sulphonated indulines dissolve with blue colour, changing to violet on dilution with water. By oxidation they yield quinone and other products, and by reducing agents are converted into unstable leuco-derivatives.

Soluble indulines are used for the preparation of coloured inks, and both the soluble and insoluble in the preparation of spirit-varnishes. They are very fast dyes, and are employed for producing grey, bluish, and blue-black shades on wool, silk, leather, etc., and are used as indigo-substitutes. In commerce they are met with under a variety of names, including, besides those already mentioned, *Blackley Blue*, *Guernsey Blue*, *Indigo-substitute*, *Bengaline*, *Coupier's Blue*, *Acetin Blue*, *Pelican Blue*, *Indigen D*, *F*, *Sloeline*, *RS*, *BS*, *Azine Blue*, *Indophenin Extra*, *Soluble Blue CB*, *Printing Blue*, *Printing Blue H*, *R*, *B*, *Bengal Blue*, *Fast Blue RR*, etc.

Commercial name	Formula	Remarks
Acetine Blue. Lævuline Blue. Printing Blue.	....	Solution of indulines in acetins. (acetic esters of glycerol).
Amethyst Violet. Iris Violet.	$(C_2H_5)_2N(4)C_6H_3 \left\{ \begin{matrix} (1).N:(1) \\ (2).N.(2) \end{matrix} \right\} C_6H_3(4):N(C_2H_5)_2Cl$ C_6H_5	....
Azindone Blue G.	By heating $CH_2[C_6H_4.N:N.C_6H_4.NH_2]_2$ for an induline melt and then rendering water soluble with *p*-phenylenediamine.	....
Azindone Blue R.	....	....
Azine Green, G B, T O.	$C_6H_5NH(6)C_{10}H_5 \left\{ \begin{matrix} (1).N:(1) \\ (2).N.(2) \end{matrix} \right\} C_6H_3(4):N(CH_3)_2Cl$ CH_5	....
Azine Green S.	Sodium salt of sulphonated azine green.	....
Azine Scarlet G.	$\left. \begin{matrix} CH_3(5) \\ NH_2(4) \end{matrix} \right\} C_6H_2 \left\{ \begin{matrix} (1).N:(1) \\ (2).N.(2) \end{matrix} \right\} C_6H_3(4):N(CH_3)_2Cl$ CH_3	....
Azocarmine B. Rosinduline 2B.	Disulphonic acid of phenylrosinduline; trisulphonic acid of phenylrosinduline as Rosinduline 2B, bluish.	....
Azocarmine G. Rosazin.	$C_8:H_{17}N_3S_2O_6Na_2$ = The sodium salt of disulphonic acid of phenyl rosinduline. $C_6H_4 \left\{ \begin{matrix} (1).N:(1) \\ (2).N.(2) \end{matrix} \right\} C_{10}H_5(4):N.C_6H_5$ C_6H_5	....
Basle Blue R, BB.	$CH_3.C_6H_4.NH(7)C_{10}H_5 \left\{ \begin{matrix} (1)N(1): \\ (2)N(1) \end{matrix} \right\} C_6H_3:(4)N(CH_3)_2Cl$ $C_6H_4CH_3$	Action of nitrosodimethylaniline on 2:7-ditolyl (or diphenyl) naphthylene-diamine.
Basle Blue S.	....	By sulphonation of Basle Blue and conversion into sodium salt.
Brilliant Induline (Kalle).	Sulphonic acids of an induline.	....

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Grey powder, violet solution.	No change.	Blue.	Green.	Blue then violet.	
Violet powder, blue solution.	Violet ppt.	Redder.	Green.	Violet.	
Brown powder, violet solution.	Violet ppt.	Redder.	Green.	Violet.	
Green powder, green solution.	Green ppt.	Green ppt.	Brown.	Green.	
Black powder, bluish-green solution.	No change.	No change.	Violet.	Green.	
Brown powder, red solution.	No change.	Red or with excess of acid; blue.	Blue-green.	Violet to red.	
Brown powder, violet solution.	No change.	Brown ppt.	green.	....	Wool dye.
Red paste. metalic lustre, bluish-red solution, difficultly soluble.	No change.	Red ppt.	Green.	Red ppt.	Wool dye.
Brown powder, violet solution.	....	Blue ppt.	Brown.	Violet ppt.	Brighter with stannous chloride and hydrochloric acid.
Coppery powder, blue solution.	....	....	Yellow.		
Dark blue powder, soluble in water.	Dull claret.	Colour weaker.	Reddish-blue solution.	....	For silk, wool, leather and dressings.

Commercial name	Fromula.	Remarks
Fast Blue R.	Sodium salts of sulphonic acids of indulines.	....
Fast Neutral Violet B.	$C_2H_5NH.C_6H_3\left\{\begin{matrix}.N:\\.N.\\\mid\\C_2H_5\end{matrix}\right\}C_6H_3:N(CH_3)_2Cl$	From nitroso-dimethylaniline and diethyl-*m*-phenylene diamine.
Flavinduline.	$C_{14}H_8\left\{\begin{matrix}:N.\\:N.\end{matrix}\right\}C_6H_4$ with Cl and C_6H_5 on N	From phenanthra-quinone and *o*-amino-diphenylamine.
Heliotrope B, 2B Tannin Heliotrope	$\left.\begin{matrix}CH_3\ (3)\\CH_3\ (6)\\NH_2\ (4)\end{matrix}\right\}C_6H\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$, $(1)C_6H_3\left\{\begin{matrix}(2)NH_2\\(6)NH_2\end{matrix}\right.$ on N	....
Indamine GG.	....	....
Indamine J and JO.	....	....
Indamine R.	....	....
Indamine 2R and 3R.	....	....
Indamine 6R.	....	....
Indamine Blue B for wool.	....	....
Indamine Blue N.	....	....
Indamine Blue N extra.	....	....
Indamine Blue NB	....	....

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Bronze powder, violet solution.	Violet ppt.	Bluer.	Blue.	Violet.	
Bronze powder, violet solution.	No change.	....	Grey.	Violet.	
Orange powder, orange solution.	Yellow ppt.	No change.	Violet.	Yellow.	
Brown paste or grey-green powder, fuchsine-red solution.	Red ppt. soluble in water.	Blue if a large excess.	Green.	Blue then red.	Dyes cotton (tannined) reddish-violet.
Gray powder, blue solution.	Ppt.	No change.	Green.	Bluer.	Soluble in alcohol.
Red powder, blue solution.	Ppt.	No change.	Green.	Turbid.	Soluble in alcohol.
Brown powder, blue solution.	Redder.	No change.	Green.	Violet.	Soluble in alcohol.
Grey powder, violet solution.	Violet ppt.	No change.	Green.	Red.	Soluble in alcohol.
Green powder, magenta-red solution.	Red ppt.	No change.	Green.	Red.	Soluble in alcohol.
....	....	Bright blue with concentrated acid.	Bright blue.	....	On the fibre turned darker by concentrated sulphuric and hydrochloric acids, a dull green by nutric acid (sp. gr. 1.40) and purple by sodium hydroxide (10%).
Grey powder, blue solution.	Violet ppt.	Bluer.	Black.	Violet.	Soluble in alcohol.
Brown powder, violet solution.	Violet ppt.	Blue.	Bluish-green	Violet.	Soluble in alcohol.
Brown powder, blue solution.	Redder.	Greener.	Green.	Blue.	Soluble in alcohol.

Commercial name	Formula	Remarks
Indamine Blue NB extra.	....	....
Indamine Blue WG.	....	....
Indamine Blue NR.	....	....
Indazine M.	$C_6H_5.NH.C_6H_3\left\{\begin{matrix}.N:\\.N.\end{matrix}\right\}C_6H_3:N(CH_3)_2Cl$ $\vert$ C_6H_5	By the action of nitroso-dimethylaniline on diphenyl-*m*-phenylene-diamine.
Indoine Blue R.	....	By diazotisation of safranine and coupling with β-naphthol.
Induline.	Induline 3B $C_{36}H_{25}N_5$. Induline 6B $C_{42}H_{32}N_6$.	By heating aminoazo-benzene with aniline and its hydrochloride.
Induline Black (Kalle).	Sulphonic acids of indulines.	....
Induline Scarlet.	$CH_3.C_6H_3\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_{10}H_6:(4)NH_2Cl$ $\vert$ C_2H_5	....
Magdala Red. Naphthalene Red.	$NH_2.(4)C_{10}H_5\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_{10}H_5:(4)NH_2Cl$ $\vert$ $C_{10}H_7$	From amino-azonaphthalene and α-naphthylamine.
Mauve Mauveine.	$C_6H_5.NH(4)C_6H_3\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_6H_3:NH_2Cl.$ $\vert$ C_6H_5	By oxidation of aniline. Perkin's "mauveine" was probably a higher homologue, $C_{27}H_{24}N_4$.
Metaphenylene Blue B.	$C_7H_7.NH.C_6H_3\left\{\begin{matrix}.N:\\.N.\end{matrix}\right\}C_6H_3:N(CH_3)_2Cl$ $\vert$ C_7H_7	By action of nitroso-dimethylaniline on ditolyl-*m*-phenylene diamine.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Coppery powder, blue solution.	Blue ppt.	No change.	Green.	Blue.	Soluble in alcohol.
Red powder, blue solution	Redder.	Darker.	Green.	Blue.	Soluble in alcohol.
Grey powder, blue solution.	Violet.	No change.	Green.	Purple.	Soluble in alcohol.
Bluish-red dyestuff.	Redder.	Blue.	Green.	Blue then violet.	
....	Pink.	....	Green.	....	Greener with stannous chloride in hydrochloric acid.
....	....	....	....	....	The higher indulines give insoluble salts with acids, hence they are generally sulphonated, or else dissolved in acetin and used for printing.
Dark blue powder, soluble in water.	Dull claret.	Colour much weaker.	Reddish-blue.	....	For silk, wool, leather and dressings.
Red powder, red solution.	Violet ppt.	....	Red.	Green to Red.	Soluble in alcohol.
Brown powder, red solution in hot water.	Violet ppt.	Blue.	Violet.	Red ppt.	Soluble in alcohol with red fluorescence.
Red solution in hot water. More easily soluble in alcohol.	Violet ppt.	No change with fairly dilute acid.	Green.	Violet after passing through blue.	
Dark powder, violet solution.	Violet ppt.	Bluer.	Grey.	Blue.	Soluble in alcohol. Dyestuff for wool. With nitric acid (sp. gr. 1.40); dull green.

Commercial name	Fromula	Remarks
Methylene Violet RRA, 3RA. Fuchsia. (Dimethyl phenosafranine.)	$NH_2.C_6H_3\left\{\begin{matrix}.N:\\.N.\end{matrix}\right\}C_6H_3:N(CH_3)_2Cl$ C_6H_5	By oxidation of 1 molecule dimethyl-*p*-phenylene-diamine with 2 molecules of aniline.
Milling Blue.	$C_6H_5NH(4).C_{10}H_5\left\{\begin{matrix}(1).N:(2)\\(1).N.(2)\end{matrix}\right\}C_{10}H_5(4):NH(C_6H_5)Cl$ C_6H_5	....
Naphthazine Blue	$C_{10}H_7NH(4)C_6H_3\left\{\begin{matrix}(1).N:(2)\\(2).N.(2)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$ $C_{10}H_7$	By action of nitrosodimethylaniline on dinaphthyl-*m*-phenylene-diamine.
Naphthyl Blue.	Sulphonated derivative of $C_6H_5.NH.C_{10}H_5\left\{\begin{matrix}.N:\\.N.\end{matrix}\right\}C_{10}H_5:N.C_6H_5$ C_6H_5	By heating Benzeneazo-phenyl α-naphthylamine with phenol.
Naphthyl Red.		
Naphthyl Violet.	$C_6H_5.NH.C_{10}H_5\left\{\begin{matrix}.N:\\.N.\end{matrix}\right\}C_{10}H_5:NH_2Cl$ C_6H_5	Produced, with naphthyl blue, by heating nitroso-β-naphthylamine with α-naphthylamine and aniline.
Neutral Blue.	$C_{10}H_6\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$ C_6H_5	....
Neutral Red. Tolylene Red.	$\left.\begin{matrix}NH_2(5)\\CH_3(4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1).N:(1)\\(2).N:(2)\end{matrix}\right\}C_6H_3(3)N(CH_3)_2$	By oxidation of dimethyl-*p*-phenylene-diamine with *m*-tolylene diamine.
Neutral Violet.	$NH_2(4)C_6H_3\left\{\begin{matrix}(1).N:(1)\\(2).N:(2)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2$	From *m*-phenylene-diamine and dimethyl-*p*-phenylene-diamine.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Dark powder, violet solution, usually double salt with $ZnCl_2$.	Brown ppt.	Bluer.	Green.	Violet.	Soluble in alcohol. Used in printing and cotton dyeing.
Bronze powder, blue solution.	Darker.	Blue ppt.	Bluish-green.	Blue.	
Bronze powder, blue solution.	Violet ppt.	No change.	Bluish-green.	Reddish blue.	Wool dyestuff. With nitric acid (sp. gr. 1.40) dark violet with stannous chloride in hydrochloric acid, a duller shade.
....	....	....	Green.	....	Silk dyed with Naphthyl Blue shows strong fluorescence; nitric acid (sp. gr. 1.40), brown-red.
....	....	....	Green.		
Brown powder, violet solution.	....	Yellowish-green if concentrated.	Yellowish-green.	Green to blue and violet.	Green with stannous chloride in hydrochloric acid.
Red solution.	Yellow.	Blue if acid is concentrated.	Green.	Blue, then rose-red.	Can be used as basic dyestuff on cotton mordanted with tannin, but sensitiveness to alkalies makes application limited.
Greenish-black powder, violet solution.	Brown ppt.	Blue with excess of acid.	Green.	Blue then violet.	

Commercial name	Formula	Remarks
Nigramine.	....	By action of nitroso-dimethyl-aniline hydrochloride on aniline hydrochloride.
Nigrosine, soluble in water (Kalle).	Sulphonic acid of induline.	....
Paraphenylene Blue R. Fast New Blue for cotton.	Probably amino-derivatives of Induline 3 B and 6 B, since the dye is produced by heating aminoazobenzene with *p*-phenylenediamine instead of aniline.	More soluble and more basic than induline.
Paraphenylene Violet.	? An amino-derivative of phenyl-rosinduline.	Action of *p*-phenylenediamine on *a*-aminoazonaphthalene.
Rhoduline Red G and B. Rhoduline Violet.	$\left.\begin{matrix}CH_3\\NH_2\end{matrix}\right\} C_6H_2 \left\{\begin{matrix}.N:\\.N.\end{matrix}\right\} C_6H_3:N(CH_3)_2Cl$ C_6H_5	....
Rosinduline G.	$C_6H_4 \left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\} C_{10}H_4 \left\{\begin{matrix}(6)SO_3Na\\(4):O.\end{matrix}\right.$ C_6H_5	A sodium sulphonate of rosindone.
Rosinduline 2G	Sodium salt of a rosindone-mono-sulphonic acid.	....
Rosolan B, R, OT in powder.	$C_6H_5.NH(4).C_6H_3 \left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\} C_6H_2 \left\{\begin{matrix}(5)CH_3\\(4):NH_2Cl\end{matrix}\right.$ $C_6H_4.CH_3$	By oxidising *p*-aminodi phenylamine with *o*-toluidine.
Rubramine	....	Action of nitroso-dimethylaniline hydrochloride on *p*- and *o*-toluidine.
Safranine. Safranine T, extra G, S, FF extra, conc., AG, AGT, OOF, GOO.	$\left.\begin{matrix}CH_3(5)\\NH_2(4)\end{matrix}\right\} C_6H_2 \left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\} C_6H_2 \left\{\begin{matrix}(5)CH_3\\(4):NH_2Cl\end{matrix}\right.$ C_6H_5	By oxidising equimolecular proportions of *p*-tolylene-diamine, *o*-toluidine and aniline.

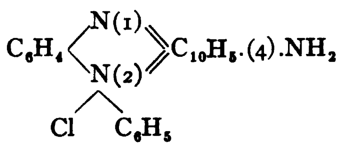
Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Black powder, violet solution.	Violet ppt.	No change.	Green.	Violet.	Soluble in alcohol.
Dark blue powder, soluble in water.	Red violet.	Greener and weaker.	Solution blue.	....	For silk, wool, leather and dressings.
Dark powder, blue solution.	Violet ppt.	Bluer.	Blue.	No change.	
Bronzy powder, violet solution.	Violet ppt.	No change.	Bluish-violet.	Blue then violet.	
Brown powder. Rhoduline violet, shining black-green powder. Red solution.	Brown ppt.	Dark ppt.	Green.	First blue, then violet, finally red.	
Red powder, red solution.	Scarlet ppt.	Yellow ppt.	Green.		
Scarlet powder, scarlet solution.	Scarlet ppt.	Yellow ppt.	Green.	Orange.	Wood dyestuff. Yellow with nitric acid (sp. gr. 1.40) and brown with stannous chloride in hydrochloric acid.
Dark powder, violet solution.	Violet ppt.	....	Green.	Eventually violet.	Soluble in alcohol.
Green powder, cerise solution.	Red ppt.	No change	Green.	Red.	Soluble in alcohol.
Brown powder, red solution.	Red ppt. with concentrated alkali.	Violet or blue.	Green.	Through blue to red.	Soluble in alcohol. Salt of a powerful base. Decolourised by warning with stannous chloride in hydrochloric acid.

Commercial name	Formula	Remarks
Safranine B Phenosafranine.	$NH_2(4)C_6H_3\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_6H_3(4):NH_2Cl$ with C_6H_5 on the (2).N	By oxidising *p*-phenylene-diamine with aniline.
Safranine MN Clemantine Giroflé.	$\left.\begin{matrix}CH_3(5)\\NH_2(4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$ with C_6H_5 on the (2).N	From aniline, *o*-toluidine and dimethyl-*p*-phenylene-diamine.
'Safranine RAE (Kalle) (Tolusafranine).	....	....
Spirit Induline (Kalle)	Hydrochlorides of indulines.	....
Spirit Nigrosine (Kalle)	Hydrochlorides of indulines.	....
Tolylene Blue B for Cotton.	?$C_6H_5NH(4)C_6H_3\left\{\begin{matrix}(1).N:(1)\\(2).N.(2)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(3)NH.C_6H_5\\(4):NH.C_7H_6.NH_2\end{matrix}\right.$ with C_6H_5 on the (2).N and Cl on the (4):NH	Action of *p*-tolylene diamine on spirit induline.
Wool Grey B, G and R.	....	Action of aniline on condensation product of nitroso-dimethylaniline with B-naphthol-sulphonic acid S.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Crystals, green reflex, red solution.	With concentrated alkali. Brown ppt. soluble in water.	Violet or blue.	Green.	Through blue to red.	Salt of a powerful base. Strongly resembles ordinary safranine.
Metallic reflex, violet solution.	Red ppt.	Blue.	Green.	Through blue to violet.	Soluble in alcohol.
Dull red powder.	....	....	Bright yellowish-green.	....	For tannin mordanted cotton.
Dark blue powder. Insoluble in water, soluble in alcohol.	Brown.*	Greener* and brighter.	Violet solution.	....	For spirit varnish. *Try solid (insoluble in water.
Dark blue powder. Insoluble in water, soluble in alcohol	Brown.*	Greener* and brighter.	Blue solution.	....	For spirit varnish. *Try solid (insoluble in water.
Violet powder, blue solution.	Brown ppt.	Precipitate.	Blue.	Ppt.	
Black powder, easily soluble.	Brown.	Ppt.	R. Blue, B. and G yellowish-brown.	Ppt.	

On the fibre, the indulines are turned somewhat bluer by hydrochloric acid, but nitric acid is almost without action (distinction from indigo). Ammonia and sodium hydroxide strip the fibre, forming reddish-violet solutions, which are decolourised by zinc powder, but the colour returns on filtering and exposing the liquid to the air. An acid solution of stannous chloride strips the fibre, and forms a green solution. Hypochlorites bleach some indulines, and turn others reddish-grey. The indulines are frequently applied in printing mixed with tannin and acetins (glycerol acetic esters). On steaming, the acetin dissolves the dyestuff, a tannin lake is produced, and the ester then undergoes hydrolysis into glycerol and acetic acid. As the latter volatilises, an insoluble lake is formed on the fibre.

Rosindulines and Rosindones.—The name rosinduline has been applied to the azine of the constitution



which is obtained by heating benzeneazo-α-naphthylamine with aniline and alcohol to 170°; its constitution is evident, seeing that it may be synthesised by the condensation of hydroxynaphthaquinone-imide and *o*-aminodiphenylamine (Kehrmann and Messinger, *Ber.*, 1891, **24**, 584, 2167). The rosinduline used in dyeing is a disulphonic derivative. Phenylrosinduline, in which one of the hydrogen atoms of the amino group is replaced by phenyl, melts at 235°; its disulphonic acid is known as "Azocarmine" and the trisulphonic acid as Rosinduline 2B.

Rosindone, $C_6H_4\left\langle\begin{matrix}N\\N(C_6H_5)\end{matrix}\right\rangle C_{10}H_5{:}O$, stands in the same relationship to rosinduline that aposafranone does to aposafranine; a sulphonic acid is technically employed under the name *Rosinduline.*

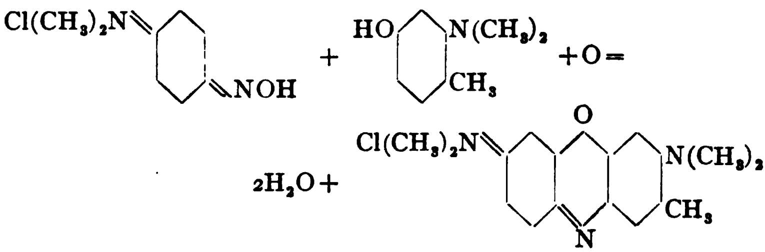
10. OXAZINES AND THIAZINES.

The oxazines are characterised by possessing a 6-membered ring consisting of 4 carbon atoms and a nitrogen and oxygen which

relatively occupy the para-position to one another. The oxazines are quinonoid in type; until recent years they were looked on as being paraquinonoid, although, as previously mentioned, Green brought forward arguments in favour of an ortho-quinonoid formulation some years ago.

F. Kehrmann (*Annalen*, 1902, **322**, 1–77, *Ber.*, 1905, **38**, 2577; 1906, **39**, 914; 1907, **40**, 613, 2071) has vigorously defended the view that the compounds of this series are to be looked on as oxonium rather than ammonium salts, while Hantzsch (*Ber.*, 1905, **38**, 2146; 1906, **39**, 153, 1365) is firmly convinced of their ammonium nature.

The oxazines are usually prepared by the action of nitrosodimethylaniline and analogous compounds on phenols. **Capri Blue,** one of the simplest members of the series, is obtained from nitrosodimethylaniline hydrochloride and dimethyl-*m*-amino-cresol.



Meldola prepared the first member of the series by the action of nitroso-dimethylaniline hydrochloride on β-naphthol.

Meldola's Blue, or **New Blue** (Cassella),[1] $C_{18}H_{15}N_2OCl$, occurs in commerce as a dark violet powder with bronze reflection. The dust strongly irritates the mucous membrane. In water it is soluble with bluish-violet colour; in alcohol with blue colour. The violet aqueous solution becomes at first green and then colourless when reduced by zinc and acetic acid, the original colour returning on exposure to air. The solution is turned blue by hydrochloric acid, and with sodium hydroxide yields a brown precipitate.[2]—In strong sulphuric acid the dye dissolves with a blackish-green colour, becomes first blue and then violet on dilution. Naphthylene Blue dyes cotton mordanted with tannin and tartar-emetic an indigo-blue colour.

[1] Also known as: *New Blue R, New Fast Blue for Cotton, Naphthylene Blue R in crystals, Cotton Blue R for Crtton, Cotton Blue R, Fast Marine Blue, Fast Cotton Blue R, RR, 3R, crystals; Phenylene Blue, Blue Nouveau P, Fast Blue III R, Fast Marine Blue RM, MM, Naphthol R and D.*

[2] If this precipitate is dissolved in sulphuric acid a group of dyestuffs called *Cyanimides* is obtained. They are colouring matters of a purple greenish-blue shade.

Muscarin, or **Campanulin,** $C_{18}H_{15}N_2O_2Cl$, introduced by Durand and Huguenin, occurs in commerce as a brown-violet powder, sparingly soluble in cold but readily in hot water, with bluish-violet colour. The solution is decolourised by heating with zinc-dust, but the colour returns on exposure to air. Hydrochloric acid produces a bluish-violet and soda a yellowish-brown precipitate. Tannin precipitates the solution with an indigo-blue colour. In concentrated sulphuric acid Muscarin dissolves with a bluish-green colour, the solution turning first blue and then violet on adding water, and on further dilution giving a violet precipitate.

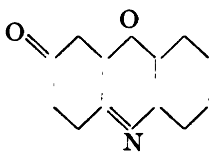
Nile Blue A is produced by the action of α-naphthylamine on the hydrochloride of nitroso-dimethyl-*m*-amino-phenol. It occurs in commerce both as the *chloride*, the formula of which has already been given, and as a *sulphate* of the composition $(C_{18}H_{16}N_3O)_2SO_4$. The *sulphate* forms a green crystalline powder with bronze reflection. It is sparingly soluble in cold water, but readily in warm, with a blue colour. It is also soluble in alcohol. The warm concentrated aqueous solution yields with hydrochloric acid needles of the chloride, which appear violet by transmitted and green by reflected light. Addition of sodium hydroxide to the dilute solution (1 : 1000) produces a red precipitate, soluble in ether to a brown-orange solution, with dark green fluorescence. Tannin in presence of sodium acetate gives a prussian-blue precipitate, and stannous chloride a dark greenish-blue precipitate, and on warming the liquid exhibits a green fluorescence, with blue transmitted light. In concentrated sulphuric acid, the dye dissolves with a yellow or red-brown colour, changing to green and blue on dilution. Wool is dyed directly by Nile Blue, a red shade of blue, and cotton mordanted with tannin and tartar-emetic is dyed blue. The colour is not fast to light, and is liable to bleed when milled with soap, but not with sodium hydroxide.

Metamine Blue B and G (*New Blue B and G, Fast Blue 2B for Cotton, Fast Cotton Blue B, Fast Marine Blue GM*, and *Naphthol Blue B*), is a dyestuff similar to Meldola's Blue, from which it is produced by condensation with dimethyl-*p*-phenylenediamine. It is dyed on cotton mordanted with tannin and tartar emetic.

Capri Blue has been already mentioned. It occurs in green crystals of the zinc chloride double salt; these are soluble in water with a blue colour. The addition of sodium hydroxide yields a blue precipitate which gives a red solution in ether, possessing a red fluorescence.

Dissolved in concentrated sulphuric acid the solution exhibits a dichroic effect; in thin layers it appears green, in thick layers red, while by transmitted gas light it appears crimson. It dyes cotton a greenish-blue on a mordant of tannin and tartar emetic, the shade being quite fast to light, soap, acids, and alkalies. It is also dyed on silk, giving a beautiful sea-green shade in artificial light.

Oxazones.—Corresponding to the oxazines, oxazones are known, the simplest being represented by the formula (Kehrmann)



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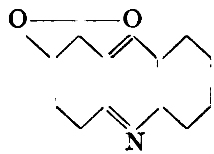
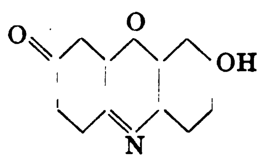


Resorufin is a hydroxy-derivative of the simplest oxazone, its formula is



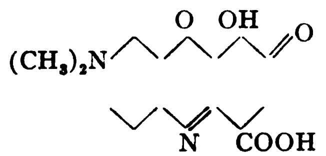
Weselsky obtained this compound by the action of nitric acid containing nitrous fumes on an ethereal solution of resorcinol; its constitution follows from its formation from nitrosophenol or quinone-chloroimide and resorcinol on the one hand, and from nitrosoresorcinol and phenol on the other. Further confirmation is afforded by its preparation when aminoresorcinol and phenol or *p*-aminophenol and resorcinol are oxidised together in sulphuric acid solution by manganese dioxide. The tetrabromo-derivative has been used technically under the name of *Fluorescent Blue*.

Fluorescent Resorcin Blue, or *Bleu fluorescent*. This dye crystallises in green lustrous needles, which are but slightly soluble in water or strong alcohol, but more readily in proof-spirit. The solutions are blue by transmitted and red by reflected light, and give a brown precipitate of hexabromresorufin on addition of a strong acid. It readily dyes silk in a neutral soap bath, the colour produced being blue, with a slight admixture of red and grey, and a characteristic red fluorescence,

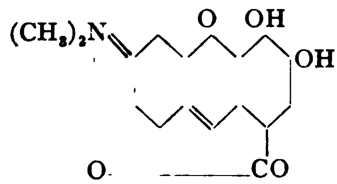
easily visible in artificial light. It is perfectly fast to light, washing, and acids, but ammonia and sodium hydroxide strip the fibre, forming blue solutions with strong red fluorescence. Strong hydrochloric acid changes the colour of fibres dyed with resorcin blue to brown.

Lacmoid.—Another blue colouring matter, sometimes called "Resorcin-Blue," can be obtained by slowly heating together 100 parts of resorcinol, 5 of sodium nitrite, and 5 of water. At 110° a vigorous reaction occurs, ammonia is evolved, and the mixture becomes red; when the melt is further heated to 115°–120° till the evolution of ammonia ceases, and the colour changes to blue. The mass is then dissolved in water and the solution filtered and precipitated by hydrochloric acid. The product is a glistening brown powder, which is insoluble in chloroform, benzene, or petroleum spirit, easily soluble in alcohol, wood spirit, and amylic alcohol, and less soluble in water and ether. The colouring matter was named by its discoverers (Traub and Hock, *J. Soc. Chem. Ind.*, 1885, **4**, 297) lacmoid, owing to its behaving to acids and alkalies in a manner analogous to litmus, with the colouring matter of which they suggested it might be identical. R. T. Thomson, however, has shown (*Chem. News*, 1885, **52**, 18 and 31) that well-marked differences exist, lacmoid being far less sensitive to weak acids than is the case with litmus. In most cases, lacmoid paper is preferable to the solution, which when used should be made with proof-spirit and of 5% strength.

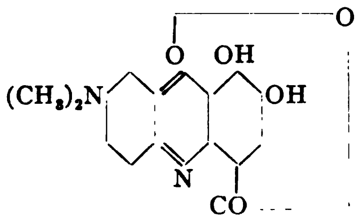
In much the same way that intermediate compounds such as safraninone exist which contain amino-groups and oxygen, thus lying between the safranines and safranones in composition and properties; so in the oxazine series corresponding intermediate products may be obtained which are produced by the condensation of compounds such as nitrosodimethylaniline with phenols and hydroxy-aromatic acids. One of the first members of this intermediate series was *Gallocyanine* obtained in 1881 by H. Köchlin by the condensation of nitrosodimethylaniline hydrochloride with gallic acid in alcoholic solution. The substance exhibits both basic and acid properties, by employing the methyl ester instead of free gallic acid, the methyl ester of gallocyanine is produced, known under the names of *Prune Pure* and *Parme R.* The hydrochloride of gallocyanine has the composition $C_{15}H_{13}O_5N_2Cl$; the free base being $C_{15}H_{12}O_5N_2$. Different constitutional formulæ have to be taken into account which represent the base as an oxazone (I) or an internal ammonium (II) or oxonium (III) salt.



I



II



III

It should be borne in mind that gallocyanine yields a diacetyl derivative which certainly is in favour of formulæ II or III.

Gallocyanine usually occurs as a greenish-grey paste; if dry it forms a bronze powder. It is generally used in conjunction with a chrome mordant for dyeing wool an indigo shade, or in cotton printing. Leuco-gallo-cyanines obtained by reduction of diverse gallocyanines are sold as 1900 *Blue*, *Deep Blue extra R*, etc. They give a violet with hydrochloric acid and their alkaline solutions rapidly oxidise on exposure to the air (blue-violet). Their chief application is in printing and dyeing on chrome mordants.

Prune forms brown crystals or powder, it is chiefly used in calico-printing.

Gallamine Blue.—If gallamide, $C_6H_2(OH)_3CONH_2$ be condensed with nitrosodimethylaniline, a corresponding dyestuff is produced which, as its bisulphite compound, is known under the name of *Gallamine Blue.* It occurs as a light grey paste, dyes chrome-mordanted wool blue and is used in calico-printing.

OXAZINE DYESTUFFS.

Commercial name	Formula	Remarks
Alizarin Green B.	$HSO_3(4)C_{10}H_5\left\{\begin{matrix}(1).N:(1)\\(2).O.(2)\end{matrix}\right\}C_{10}H_4\left\{\begin{matrix}(3)OH\\(4):O\end{matrix}\right.$	....
Alizarin Green G.	$HSO_3(6)C_{10}H_5\left\{\begin{matrix}(1).N:(1)\\(2).O.(2)\end{matrix}\right\}C_{10}H_4\left\{\begin{matrix}(3)OH\\(4):O\end{matrix}\right.$	....
Azurine.	$\left.\begin{matrix}HO_2C(4)\\HO(6)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$	....
Capri Blue G N.	$\left.\begin{matrix}(CH_3)_2N(4)\\CH_3(5)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$	....
Celestine Blue B. Coreïne RR	$\left.\begin{matrix}HO(3)\\HO(4)\\NH_2.CO(6)\end{matrix}\right\}C_6H\left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\}C_6H_3(4):N(C_2H_5)_2Cl$	....
Coreïne.	....	....
Coreïne A B, AR.	....	....
Delphine Blue.	$(CH_3)_2N(4)C_6H_3\left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\}C_6H\left\{\begin{matrix}(3)OH\\(4):O\\(6).NH.C_6H_4.SO_3NH_4\end{matrix}\right.$	By heating gallocyanine with aniline and subsequent sulphonation.
Fast Black. Fast Blue-Black.	$Cl(CH_3)_2N.(4)C_6H_3\left\{\begin{matrix}(2).O.(2)\\(1).N.(1)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(5).N:(1)\\(4).N.(2)\end{matrix}\right\}C_6H_3(4):N(CH_3)_2Cl$	....
Fast Green M.	....	Action of aniline on Muscarine.
Fluorescent Blue. Resorcin Blue. Iris Blue.	$\left.\begin{matrix}NH_4.O.(4)\\Br(3)\\Br(5)\end{matrix}\right\}C_6H\left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\}C_6H\left\{\begin{matrix}(4):O\\(3)Br\\(5)Br\end{matrix}\right.$	By bromination of resorufin.

OXAZINE DYESTUFFS.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Greenish-black powder, green solution.	Green ppt.	Red ppt.	Violet.	Red ppt.	Chrome dye for wool.
Brown-black powder, green solution.	Violet ppt.	Bordeaux ppt.	Bluish-green.	Red ppt.	Chrome dye for wool.
Black paste, violet solution in hot water.	Violet solution with paste.	Cerise solution with paste.	Blue.	Cerise.	Soluble in alcohol.
Green crystals blue solution.	Blue ppt.	Red.	Green.	Red.	Soluble in alcohol. With nitric acid (sp.gr.1.40) moss-green.
Greenish-black powder, violet solution.	Violet.	Cerise.	Blue.	Cerise.	Soluble in alcohol.
Green powder, blue solution.	Precipitate.	Red.	Blue.	Red.	Chrome dye for wool.
Blue paste, blue solution.	Bluer.	Precipitate Red.	Bordeaux Red.	Carmine.	Yellowish-brown with nitric acid (sp. gr. 1.40), With stannous chloride in hydrochloric acid; feebler.
Brown powder, violet solution.	More violet.	Redder.	Red violet.	Blue ppt.	Nitric acid (sp. gr. 1.40); brown. Stannous chloride in hydrochloric acid; somewhat weaker.
Black powder, violet-black solution.	Black ppt.	Black ppt.	Black solution.	Violet-black.	Soluble in alcohol with blue-black colour.
Brown powder insoluble in water, soluble in acetic acid.	Red ppt.	Brown.	Violet.	Orange.	
Red paste and green crystals, violet solution with green fluorescence.	No change.	Brown ppt.	Blue.	Brown ppt.	

Commercial name	Formula	Remarks
Gallamine Blue.	$(CH_3)_2N{:}(4)C_6H_3\left\{\begin{matrix}(2).O.(2)\\(1).N{:}(1)\end{matrix}\right\}C_6H\left\{\begin{matrix}(3)OH\\(4){:}O\\(6)CONH_2\end{matrix}\right.$	From gallamic acid and nitroso-dimethylaniline.
Gallanilic Green. Fast Green G.	....	By nitration of gallanilic *blue*, product of interaction of aniline and Gallamine Blue.
Gallanilic Indigo P and PS.	....	By sulphonation of gallanilic blue.
Gallanilic Violet BS.	....	....
Gallazine A	....	....
Gallocyanine. Solid Violet, etc.	$(CH_3)_2N(4){:}C_6H_3\left\{\begin{matrix}(2).O.(2)\\(1){:}N.(1)\end{matrix}\right\}C_6H\left\{\begin{matrix}(3)OH\\(4)OH\\(5).CO\end{matrix}\right.$ O (base.)	Condensation of gallic acid with nitroso-dimethylaniline.
Meldola's Blue. New Blue R. Fast Marine Blue RM, etc.	$C_{10}H_6\left\{\begin{matrix}(2).O.(2)\\(1).N\cdot(1)\end{matrix}\right\}C_6H_3(4){:}N(CH_3)_2Cl+ZnCl_2$	From nitroso-dimethylaniline and β-naphthol.
Metamine Blue B. New Blue, B, G. Fast Marine Blue G, BM, GM., etc.	$(CH_3)_2N(1)C_6H_4(4)NH(4)C_{10}H_5\left\{\begin{matrix}(2).O.(2)\\(1).N{:}(1)\end{matrix}\right\}C_6H_3(4){:}N\text{-}(CH_3)_2Cl$	By action of dimethyl-*p*-phenylenediamine *on* Meldola's Blue.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Grey paste, blue solution.	Violet.	Red.	Grey.	Red.	Chrome dye for wool.
Brown paste or powder, bluish-green solution.	Green ppt.	Blue ppt.	Carmine.	Brown ppt.	With nitric acid (*sp. gr.* 1.40); brownish-yellow. Brighter with stannouschloride in hydrochloric acid.
Blue paste. copper lustre. P. insoluble. PS. soluble.	PS. Violet solution.	P S. Dark brown ppt.	PS. Brown-violet.	PS. ppt.	
Black paste, blue solution.	Violet.	Red.	Red.	Claret.	
Brown paste, sparingly soluble.	Violet solution.	Red ppt.	Blue.	Violet ppt. and violet solution.	With nitric acid (sp. gr. 1.40); brownish-yellow. With stannous chloride in hydrochloric acid; weaker.
Grey paste or bronze powder.	Dissolves with reddish-violet colour.	Difficultly soluble in excess of hydrochloric acid. Red-violet solution.	Blue solution.	Cerise.	Forms a slightly coloured crystalline compound with sodium bisulphite. With nitric acid (sp.gr. 1.40); red-brown. *Chromocyanine*, etc., obtained by the action of sulphite on various gallocyanines are sold in paste. Printed with chrome.
Violet powder, violet-blue solution.	Brown.	Reddish.	Blackish.	Blue.	With stannous chloride in hydrochloric acid; first green, then decolourised.
Violet powder, blue solution.	Brown ppt.	Violet.	Green.	Tint dirty violet, then blue.	

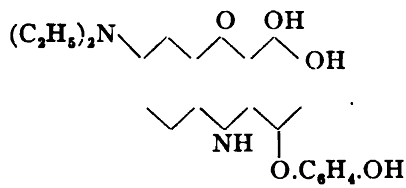
Commercial name	Formula	Remarks
Muscarine.	$HO(7)C_{10}H_4 \left\{\begin{matrix}(2).O.(2)\\(1).N:(2)\end{matrix}\right\} C_6H_3(4):N(CH_3)_2Cl$	Condensation nitroso - dimethylaniline with 2:7-dihydroxy - naphthalene.
New Methylene Blue GG.	$(CH_3)_2N.(4)C_{10}H_5 \left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\} C_6H_3(4):N(CH_3)_2Cl$	By action of dimethylamine on Meldola's Blue.
New Methylene Blue GS.		
Nile Blue.	$NH_2(4)C_{10}H_5 \left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\} C_6H_3(4):N(CH_3)_2Cl$	By condensation of nitrosodimethyl- (or diethyl-)*m*- aminophenol with *a*-naphthylamine.
Nile Blue A.	$NH_2(4)C_{10}H_5 \left\{\begin{matrix}(2).N.(2)\\(1).N:(1)\end{matrix}\right\} C_6H_3(6):N(C_2H_5)_2\frac{SO_4}{2}$	....
Nile Blue 2 B.	$C_7H_7NH.(4)C_{10}H_5 \left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\} C_6H_3(4):N(C_2H_5)_2Cl$	....
Phenocyanine.	$(CH_3)_2N.C_6H_3 \left\{\begin{matrix}(2).O.(2)\\(1).N:(2)\end{matrix}\right\} C_6H \left\{\begin{matrix}(3)OH\\(4):O\\(6).O.C_6H_4OH\end{matrix}\right.$ $?(6).C_6H_3(OH)_2$	Condensation of resorcinol with gallocyanine.
Prune Pure. Parme R (Paste).	$Cl(CH_3)_2N:(4)C_6H_3 \left\{\begin{matrix}(2).O.(2)\\(1).N:(1)\end{matrix}\right\} C_6H \left\{\begin{matrix}(3)OH\\(4)OH\\(6)COOCH_3\end{matrix}\right.$	Condensation of methyl ester of gallic acid with nitrosodimethylaniline.
Indalizarin R, J.	....	Action of sulphite on sulphonated gallocyanines.
Indalizarin green.	....	Action of nitric acid on indalizarin.

Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Brown powder, violet solution.	Brown; soluble in excess of sodium hydroxide but not in ammonia.	Blue.	Green.	Blue then violet.	With nitric acid (sp. gr. 1.40) violet-red. Colour discharged by stannous chloride in hydrochloric acid.
Grey powder, blue solution.	Green ppt.	Green.	Red-brown solution.	First brown, then green and finally blue.	Dyes silk and tannined cotton greenish-blue.
Bronze crystals, blue solution.	Red ppt.	Greenish-yellow.	Yellow.	Green then blue.	
Green crystalline powder, bronze lustre, blue solution.	Red ppt.	Ppt. of hydrochloride.	Brown.	Green then blue.	
Green powder, blue solution.	Red ppt.	Small amount; red-violet ppt., excess of acid brown solution.	Brown-red solution.	Violet ppt.	
Green paste, soluble in water.	Dissolves in alkalies with brown colour, blue on exposure.	....	Pale brown solution turning blue by exposure (oxidation).	....	Nitric acid (sp. gr. 1.40) brownish-yellow. Brighter with stannous chloride and hydrochloric acid. Phenocyanine TV by sulphonation. Phenocyanine TC by oxidation.
Brown powder or paste, violet solution.	Brown ppt.	Cerise.	Blue.	Cerise.	Chiefly used in cotton printing
Paste. Olive-coloured solution.	Brown solution, blue on exposure.	....	Pale bordeaux colour.	....	Dyed or printed on chrome-mordanted goods.
....	....	Ppt.	....	Dark reddish violet.	Fast green on chromed wool.

Delphine Blue.—When gallocyanine is heated with aniline, the carboxyl group is displaced and its place taken by an anilino-residue $.NHC_6H_5$. Sulphonation of the newly added nucleus is possible, and the ammonium salt of the monosulphonic acid comes into commerce under the name of *Delphine-Blue*. The dye gives indigo-blue shades fast to light and milling on chromed wool, while it is also used in calico-printing with a chrome mordant. The solution of the dyestuff in concentrated sulphuric acid is reddish violet; dilution of this solution occasions a dark blue precipitate.

By the action of sulphites on gallocyanine-sulphonic acids, Durand and Huguenin prepare *Indalizarine R* and *J*, from which *Indalizarine Green* is prepared by the action of nitric acid.

Phenocyanines.—Durand and Huguenin prepare a (leuco) dyestuff *Phenocyanine VS* by the action of resorcinol on the gallocyanine derived from diethylaniline and gallic acid. From Möhlau's work this compound probably has the constitution

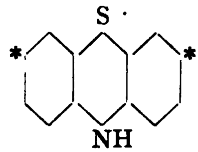


It forms an easily soluble greenish paste which gives a fine fast blue when printed on cotton with a chrome mordant. The pale brown solution in concentrated sulphuric acid slowly becomes blue by oxidation.

The oxidation product which may be looked upon as the corresponding oxazone is known as *Phenocyanine TC*, and the sulphonation of this latter compound by heating with sulphites gives rise to *Phenocyanine TV*.

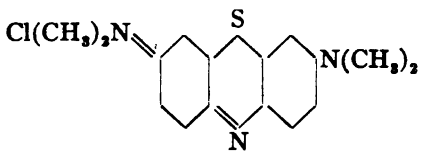
Alizarin Greens G and B are obtained by the condensation of β-naphthaquinone-sulphonic acid with 1-amino-2-naphthol-6-sulphonic acid and 2-amino-1-naphthol-4-sulphonic acid respectively. Both dye green on chrome mordants; Mark G gives a bluish-green solution in concentrated sulphuric acid going blue and violet successively on dilution and finally giving a red precipitate. Mark B gives a dull bluish-violet solution in concentrated sulphuric acid going yellowish-green on dilution and then a red precipitate.

Thiazines.—These dyestuffs are derived from a parent substance, thiodiphenylamine,



which is obtained when diphenylamine is heated with sulphur. The diamino-derivative with the two amino-groups in the different nuclei situated para to the imino-group of the thiazine ring* is the leuco-base of Lauth's Violet which may be obtained from the diaminothiodiphenylamine on oxidation. The colouring matter is also formed when an aqueous solution of *p*-phenylenediamine hydrochloride is treated with hydrogen sulphide and then oxidised with a solution of ferric chloride; the reaction may be used as a test for *p*-diamines in which one of the amino-groups happens to be primary. The reaction also furnishes an excellent confirmatory test for *p*-dinitro-compounds, *p*-nitroanilines, nitroso-dialkylanilines or other substances which furnish *p*-diamines on reduction. In such cases boil the substance under examination with tin and hydrochloric acid, dilute with water, pour off from excess of tin, saturate with sulphuretted hydrogen, filter off from tin sulphide and to the clear filtrate add ferric chloride solution drop by drop. A violet colouration is produced if the substance reduced has furnished *p*-phenylenediamine (from *p*-dinitrobenzene, *p*-nitroaniline or amino-azobenzene); if, however, the solution contains an alkylated *p*-phenylenediamine, such as is obtained by reduction of nitroso-dimethylaniline, butter yellow, etc., the colour will be blue. While Lauth's Violet is of no technical importance its tetramethyl-derivative is the dyestuff known as methylene blue.

Methylene Blue.—Methylene Blue



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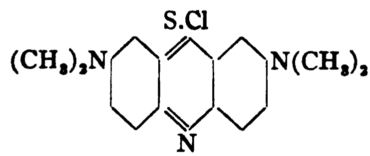
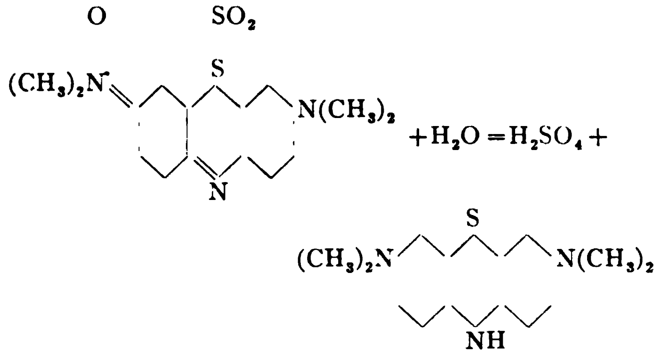


was formerly obtained by reducing an acid solution of nitroso-dimethylaniline with hydrogen sulphide or zinc dust, and then oxidising by ferric chloride in presence of a known excess of hydrogen sulphide. The colouring matter was then salted out with common salt and zinc chloride.

This process has been replaced by one in which a mixture of dimethyl-*p*-phenylenediamine and dimethylaniline are oxidised to an indamine in presence of thiosulphates. Instead of obtaining tetramethylindamine (Bindschedler's Green), a thiosulphonic derivative is formed which may be looked on as an internal salt. This compound when heated with dilute acids splits off sulphuric acid giving leucomethylene blue.



Methylene Blue[1] occurs in commerce as a hydrochloride, but more frequently as the double zinc salt. It forms a dark blue or reddish-brown powder with a bronze reflection. In water or alcohol it dissolves easily with a blue colour. The solution is not changed or is turned greenish by hydrochloric acid. Sodium hydroxide changes the colour to violet, and the addition of strong alkali to a concentrated solution produces a dirty blue or violet-black precipitate. In concentrated sulphuric acid, Methylene Blue dissolves with a grass-green colour, which, on addition of water, becomes first blue and then violet.

From a solution of commercial methylene blue, the iodide, $C_{16}H_{18}N_3$-SI is completely precipitated on adding iodide of potassium, and potassium dichromate also completely precipitates the solution as a purple-violet chromate. Methylene Blue forms a soluble compound with tannin which is taken up by metallic mordants.

[1] Also known as: *Methylene Blue B, BG* and *BB; Methylene Blue IaD and extra D; Ethylene Blue*. The latter is a mixture of Methylene Blue with Methylene Azure.

By treating Methylene Blue with zinc and acetic acid, or with an alkaline solution of sodium hyposulphite, the leuco-derivative, $C_{16}H_{19}N_3S$, is obtained. This substance crystallises from ether in flat satiny needles, having a penetrating odour resembling that of the lobster. It is readily soluble in water, and is extremely oxidisable both in the dry state and in solution, methylene blue and other products being formed. In acid solution, tetramethyl-leucothionine is more stable, and it forms a readily soluble and crystallisable double zinc salt.

The formation of methylene blue affords the most delicate and certain reaction for the detection of hydrogen sulphide in neutral or acid solution, far exceeding in this respect the reactions with lead salts and nitroprussides. 100 c.c. of the liquid to be tested should be treated with 2 c.c. of fuming hydrochloric acid, and a few grains of dimethyl-*p*-phenylene-diamine sulphate added. On then adding a drop or two of ferric chloride solution, methylene blue will be formed either immediately or on standing, if any hydrogen sulphide was previously present.

Methylene Blue is a valuable dye for cotton yarn and calico-printing. The blue produced has a greenish shade, especially in artificial light. The colour is faster than Aniline Blue, being unaffected by light and not acted on by neutral soap solution or dilute hypochlorites. Ammonia is also without action, but alkaline soaps and alkali hydroxides remove the colour. On treating the fabric with hydrochloric acid, it is turned green and the dye is gradually removed, the acid liquid remaining green. Stannous chloride and other reducing agents discharge Methylene Blue more rapidly than other blue dyes. A 3% solution of potassium dichromate changes a fabric dyed with Methylene Blue to violet, and finally discharges it. If the dye was mordanted with tannin, a dark brown colour remains.

The behaviour of methylene blue with reducing agents and the sensitiveness of the resultant leuco-derivative render the colouring matter of great value in bacteriological research. "The bacilli of tuberculosis, glanders, and cholera were first discovered by the aid of methylene blue."

Methylene Blue is reduced by phenylhydrazine at the ordinary temperature, giving the leuco-compound in a very pure form (m. p. 185°). The leuco-compound is not oxidised even by pure oxygen in an atmosphere free from acid, and in strongly alkaline solutions it is not acted upon by permanganate or hydrogen peroxide. (P. Landauer and H. Weil, *Ber.*, 1910, **43**, 198).

THIAZINE DYESTUFFS.

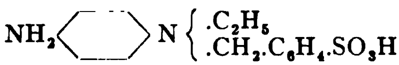
Commercial name	Formula	Remarks
Brilliant Alizarin Blue G.	$(CH_3)_2N(4)C_6H_3\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_{10}H_3\left\{\begin{matrix}(4){:}O\\(3)OH\\(7)SO_3Na\end{matrix}\right.$	....
Brilliant Alizarin Blue G. R.		
Brilliant Alizarin Blue R.	$\left.\begin{matrix}C_6H_5\\HSO_3.C_6H_4.CH_2\end{matrix}\right\}N.(4)C_6H_3\left\{\begin{matrix}(2).S.(2)\\(1).N:(1)\end{matrix}\right\}C_{10}H_4\left\{\begin{matrix}(4){:}O\\(3)OH\end{matrix}\right.$	....
Gentianine.	$NH_2(4)C_6H_3\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_6H_3(4){:}N(CH_3)_2Cl$	....
Lauth's Violet.	$H_2N(4)C_6H_3\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_6H_3(4){:}NH_2Cl$	Oxidation of *p*-phenylene-diamine in presence of hydrogen sulphide.
Methylene Blue B.	$(CH_3)_2N.(4)C_6H_3\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_6H_3(4){:}N(CH_3)_2Cl$	Commercial article usually the double zinc chloride.
Methylene Green G.	$\left.\begin{matrix}NO_2\\(CH_3)_2N\end{matrix}\right\}C_6H_2\left\{\begin{matrix}.S.\\.N:\end{matrix}\right\}C_6H_3.N(CH_3)_2Cl$	Nitration of methylene blue.
New Methylene Blue N.	$\left.\begin{matrix}CH_3.(3)\\C_2H_5.NH.(4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(3).CH_3\\(4){:}NH(C_2H_5)Cl\end{matrix}\right.$	....
Thiocarmine R.	$\left.\begin{matrix}C_2H_5\\SO_2.C_6H_4.CH_2\end{matrix}\right\}N{:}(4)C_6H_3\left\{\begin{matrix}(2).S.\ (2)\\(1){:}N.\ (1)\end{matrix}\right\}C_6H_3(4)\left.\right\}.N\left\{\begin{matrix}C_2H_5\\SO_3Na.C_6H_4.H_2C\end{matrix}\right.$ (with SO_2 joined to O on N)	From ethylbenzylamine sulphonic acid.
Thionine Blue G.		
Thionine Blue G, O extra.	$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}N.(4)C_6H_3\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_6H_3(4){:}N(CH_3)_2Cl$	....
Toluidine Blue O.	$\left.\begin{matrix}CH_3(5)\\NH_2(4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(2).S.\ (2)\\(1).N:\ (1)\end{matrix}\right\}C_6H_3(4){:}N(CH_3)_2Cl$	....
Urania Blue.	....	Oxidation of β-dinaphthyl-*m*-phenylene-diamine-disulphonic acid with dimethyl-*p*-phenylene diamine thiosulphonic acid.

THIAZINE DYESTUFFS.

Character of dyestuff	Reaction of aqueous solution		Reaction of dye with sulphuric acid		Other characteristics
	With sodium hydroxide	With hydrochloric acid	With conc. acid	On dilution with water	
Brown paste, blue solution.	Violet.	Violet ppt.	Green.	Violet.	Nitric acid (sp. gr. 1.40); yellow. Decolourised by stannous chloride in hydrochloric acid.
Black paste.	....	Green.	Green.	Violet.	
Red Brown powder, bluish-violet solution.	First a more violet colouration then ppt.	Greener.	Yellowish-green solution.	First blue, then blue-violet.	
Hydrochloride: needles with cantharidine lustre. Violet solution	Ppt.	....	Green.	Blue then violet.	Not employed as a dyestuff.
Dark blue or brown powder, blue solution.	The base, liberated by moist silver oxide is easily soluble in water with blue colour.	....	Green.	Blue.	Decolourised by stannous chloride in hydrochloric acid.
Brown powder, green soution.	Violet.	Greener.	Dark Green.	Bluish-green.	Reduction gives a leuco-compound which reoxidises to a blue dyestuff.
Metallic powder, blue solution.	Red-brown ppt.	Green with concentrated acid in excess.	Green.	Blue.	Decolourised by stannous chloride in hydrochloric acid.
Blue powder, blue solution.	No change in cold. Violet on heating.	No change.	Yellowish-green.	Blue.	
Brown powder, blue solution.	Violet.	No change.	Yellowish-green.	Blue.	
Green powder, violet solution.	Dirty violet ppt.	Blue.	Yellowish-green.	Blue.	
Violet powder with bronze lustre, blue solution.	No change.	Dark blue (soluble) ppt.	Brownish-green solution.	Blue.	Dyes wool and silk from an acid bath.

Nitration of methylene blue yields *Methylene Green* which is a mononitro-derivative. It form a dark brown powder which gives a dark green solution in concentrated sulphuric acid going blue on dilution (Gnehm and Walder, *Ber.*, 1906, **39**, 1020; Grandmougin and Walder, *Zeit. Farben-Ind.*, 1906, **5**, 285).

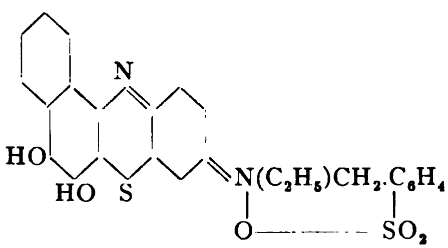
Thiocarmine R (Cassella) is an acid dyestuff of the series obtained by oxidation of thiosulphates and benzyl-ethyl-*p*-phenylene-diamine sulphonic acid



It gives a grass green solution in concentrated sulphuric acid, going bright blue on dilution; it dyes wool and silk from an acid bath.

Mixed dyestuffs with different rings or groupings on either side of the thiazine ring may be obtained by the thiosulphate process; this may be illustrated by reference to *Brilliant Alizarin Blue.*

Brilliant Alizarin Blue G and R (Bayer), or **Indochromine T** (Sandoz).—Under this name sulphonic derivatives of substituted naphtho-phenthiazines are placed on the market. When benzyl-ethyl-*p*-phenylene-diamine sulphonic acid is oxidised in presence of thiosulphates a thiosulphonic acid is obtained. Subsequent condensation with *β*-naphthaquinone and elimination of sulphuric acid leads to the production of the dyestuff which may be represented by the formula



The dye gives a very fast blue on chromed wool, cotton and silk; it may be used for calico-printing. The use of *Indochromogen S* has already been referred to.

11. QUINOLINE AND ACRIDINE DYESTUFFS.

Several dyestuffs (amino-derivatives) related to acridine have found extensive use in dyeing, but quinoline derivatives may be dismissed

somewhat briefly as lack of fastness or expense have hindered any considerable employment.

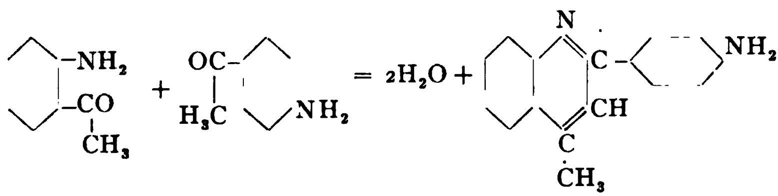
Cyanine or Quinoline Blue, $C_{29}H_{35}N_2I$, is obtained by heating a mixture of quinoline and lepidine with an alkyl iodide in the presence of an alkali. It is a strongly basic compound and its mono-acid salts occur as beautiful blue crystals. It is not important as a dyestuff, as the shades obtained with it are very sensitive to light and acids. It is insoluble in cold water, and only slightly so in hot water, giving a violet-blue solution which smells of quinoline. With strong sulphuric acid it evolves iodine on heating. This dyestuff has found application in the preparation of isochromatic photographic plates.

Quinoline red is a similar substance obtained by the action of benzo-trichloride on quinoline in the presence of zinc chloride.

It occurs as small brownish-red needles, insoluble in cold water, though fairly soluble on warming. In alcohol it yields a red solution exhibiting an orange fluorescence. It is not employed to any extent as a dyestuff, but finds a similar use to cyanine, a mixture of the two constituting the so-called *Azalin.*

Flavaniline, $C_{16}H_{14}N_2$,HCl.—When acetanilide is heated with zinc chloride to a temperature of 250°–270°, it is converted into a colouring matter, the free base of which has the constitution of a *p*-aminophenyl-γ-lepidine. The mechanism of the reaction has been explained by the researches of O. Fischer and Bedall (*Ber.*, 1882, **15,** 684), Fischer and Rudoff (*Ibid.*, **15,** 1500), Fischer and Besthorn (*Ber.*, 1883, **16,** 68), Fischer and Täuber (*Ber.*, 1894, **17,** 2925).

The first effect of the zinc chloride is to isomerise the acetanilide to a mixture of *o*- and *p*-amino-acetophenones which then condense in the following manner:



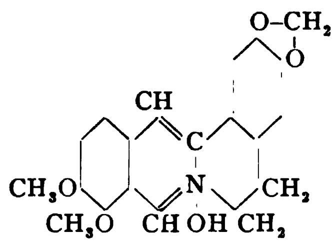
Flavaniline is now almost obsolete in commerce. It is a hydrochloride of the base, and occurs as an orange-yellow crystalline powder, readily soluble in water with a yellow colour. The solution is unchanged by hydrochloric acid, but on adding sodium hydroxide

yields a milky precipitate of the free base, soluble in ether, without colour, but with a steel-blue fluorescence. In strong sulphuric acid, flavaniline dissolves with a dirty-yellow colour and blue fluorescence. Flavaniline dyes wool and silk yellow without a mordant. Silk dyed with flavaniline exhibits a fine moss-green fluorescence.

Flavaniline S is a sulphonated flavaniline. It resembles the basic dye, but the solution is gradually decolourised by sodium hydroxide without a precipitate being formed. In strong sulphuric acid it forms a colourless solution, becoming yellow on dilution.

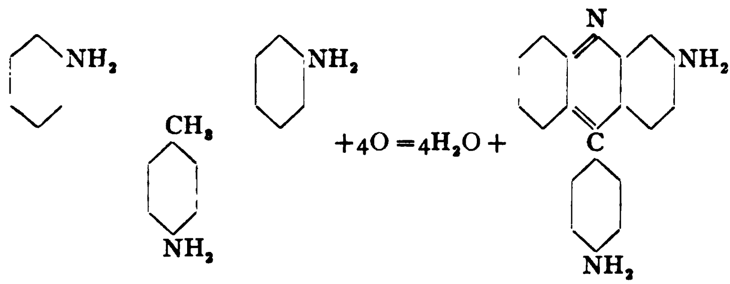
Quinoline Yellow (or Quinophthalon), $C_{18}H_{11}O_2N$, is obtained by heating quinaldine with phthalic anhydride and zinc chloride.

The product forms a yellow powder, which is insoluble in water, but difficultly soluble in alcohol, to form a yellow solution. In strong sulphuric acid the dye dissolves with a yellowish-red colour, the solution giving a flocculent yellow precipitate on dilution. By sulphonation, Quinoline Yellow yields a disulphonic acid, the sodium salt of which is known as *Water-soluble Quinoline Yellow.* It forms a bright yellow powder dissolving easily in water with an intense yellow colour, which is unaltered by dilute acids but which is turned somewhat darker by ammonia. The dye is not applicable to cotton. On silk and wool, in a bath acidified with sulphuric acid, it yields very pure shades of yellow, which stand light fairly well. *Berberine*, $C_{20}H_{17}O_4N$, a natural yellow dyestuff found in *Berberis vulgaris*, etc. (see Vol. 6), must be classed with isoquinoline derivatives, since W. H. Perkin has shown that its constitution is to be expressed by the formula

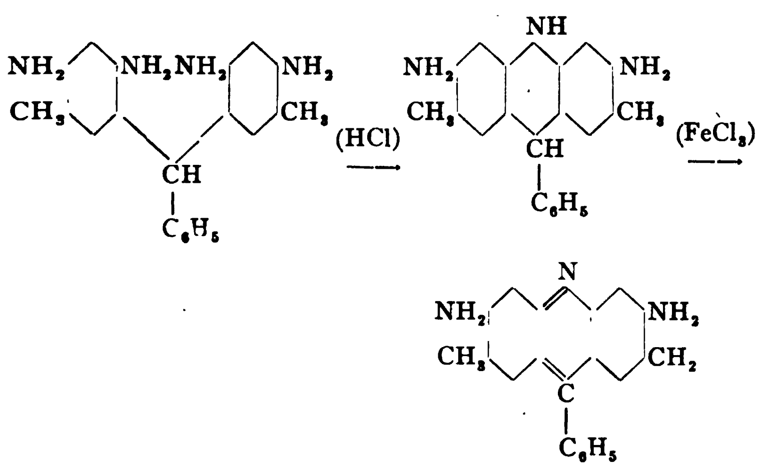


Acridine Dyes.—The acridine dyes are of much greater importance than those derived from quinoline. One of them, *Aniline Yellow* or *Chrysaniline* has been known for a long time as a bye-product formed in the manufacture of magenta; it is an unsymmetrical diamino-

acridine and owes its formation to the condensation of 1 molecule of *p*-toluidine with 2 molecules of aniline in the following manner:

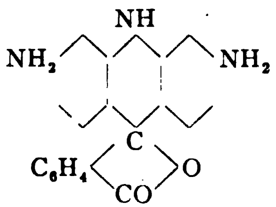


Most of the dyestuffs of this series in use at the present time are obtained from *m*-diamines which condense with aldehydes forming derivatives of tetra-amino-triphenylmethane. On heating these with hydrochloric acid under pressure, ammonia is eliminated and a dihydro-acridine produced from which the dyestuff is formed on oxidation with reagents such as ferric chloride. The production of benzoflavine, a typical member of the series, illustrates the method; the following scheme assumes that tetra-amino-dimethyltriphenylmethane has already been formed by the condensation of 1 molecule of benzal dehyde with 2 molecules of *m*-tolylene-diamine

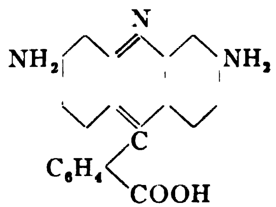


It may be noted that substituted benzaldehydes can be employed for the condensation; on the other hand *m*-phenylene-diamine does not condense as smoothly as tolylene-diamine, although *m*-amino-dimethylaniline gives a clean reaction. In fact, Acridine Orange, which is a tetramethyldiamino-acridine, is obtained from *m*-amino-dimethylaniline and formaldehyde by reactions similar to those by which benzoflavine is obtained from *m*-tolylenediamine and benzaldehyde.

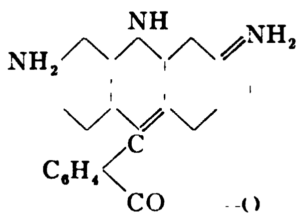
Fluoresceïn on prolonged heating under pressure with ammonia has its hydroxyl-groups replaced by amino-groups and its pyrone oxygen atom by an imino-group (R. Meyer, *Ber.*, 1888, **21**, 3376). The resulting compound may be looked on either as a derivative of phthalide (I), as a diaminophenylacridine-carboxylic acid (II), or as an internal quinonoid betaïne (III).



I



II



III

Similar remarks as to constitution apply in the case of *flaveosin*, which is a tetra-alkylated derivative of the compound just mentioned.

Benzoflavine is a yellow substance soluble with difficulty in cold water, but more readily on heating. It is precipitated from its aqueous solution by dilute acids. In strong sulphuric acid it dissolves with yellow colour and pronounced yellowish-green fluorescence. The alcoholic solution shows an intense yellowish fluorescence, which disappears on the addition of an acid. The free base of benzoflavine is colourless and insoluble in water, but soluble in alcohol and ether. Benzoflavine is chiefly dyed on the cotton fibre, for which purpose the material is mordanted with tannin and tartar emetic. It yields a very

pure yellow shade which is quite fast to soap and light. It is mostly used for shading malachite green and safranine, and in calico-printing.

Acridine Orange, $C_{17}H_{19}N_3,HCl+ZnCl_2$, is the zinc chloride double salt of tetramethyldiamino-acridine. It is a basic dyestuff resembling chrysaniline. Its solution in water and alcohol is orange in colour and exhibits a green fluorescence. It gives orange shades on mordanted cotton which are very fast to soap. It is also used for dyeing leather, to which it imparts a peculiar golden lustre.

Chrysaniline. Phosphine.—This colouring matter, also called *Aniline Yellow*, *Aniline Orange*, and *Leather Yellow*, *Philadelphia Yellow G*, *Xanthin*, *Leather Brown*, *Phosphine II*, *N*, and *P*, *Patent Phosphine* and *Nankin*, is obtained as a secondary product of the manufacture of magenta.[1]

Commercial *Phosphine* forms an orange-yellow powder, readily soluble if the hydrochloride, but difficultly if the nitrate, to a reddish-yellow solution. It is also soluble in alcohol. Dilute hydrochloric acid simply deepens the colour, but with excess of the strong acid a dihydrochloride is precipitated, readily soluble in pure water. Ammonia and sodium hydroxide liberate free chrysaniline as an amorphous yellow precipitate, which melts on boiling, the liquid being coloured pale yellow. The precipitate is soluble in ether. Phosphine dissolves in strong sulphuric acid to form a reddish-yellow solution which exhibits a strong green fluorescence. On dilution, a reddish-yellow solution is obtained.

On adding nitric acid or sodium nitrate to a tolerably concentrated solution of phosphine, the sparingly soluble chrysaniline nitrate separates as a red crystalline precipitate. In warm solutions, the precipitate is produced slowly, and on stirring the liquid is deposited in streaks in the track of the glass rod. Under the microscope the precipitate is seen to consist of needles. This characteristic reaction, when carefully applied, distinguishes phosphine from other yellow colouring matters, but is liable to fail in solutions of the nitrate. Hence a preferable plan is to liberate the base by ammonia, agitate with ether, treat the separated ethereal solution with dilute acetic acid, concentrate the acetic solution,

1 The resinous bye-products contain chrysaniline, mauvaniline, violaniline, a little rosaniline, and undefined resinous matters. On boiling the mass with dilute hydrochloric acid, resins and violaniline remain insoluble. By fractional precipitation of the filtered solution with lime, mauvaniline, rosaniline, and chrysaniline are successively precipitated. Chrysaniline may be more easily prepared from the mother-liquors which remain after precipitating the magenta by salt, in the arsenic acid process. More salt is added to the liquid and then lime, the precipitate treated with dilute nitric acid, and the sparingly soluble nitrate of chrysaniline precipitated by adding excess of nitric acid to the solution.

and add sodium nitrate. This mode of operating excludes the possibility of confusion with nitro-compounds, which often yield yellow crystalline precipitates on treating their solutions with nitric acid or potassium nitrate. But the nitro-dyes are not extracted by agitating their ammoniacal solutions with ether, though, unlike chrysaniline, most of them are extracted from their acidified solutions. Nitro-compounds are further distinguished by the red or brownish colour developed on boiling with potassium cyanide; whereas phosphine gives a yellow precipitate in the cold, and the liquid acquires a yellow colour on boiling.

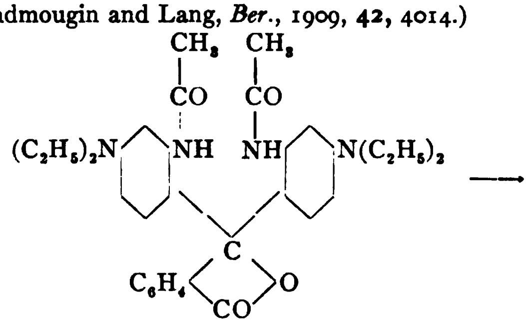
On treatment with stannous chloride and hydrochloric acid, chrysaniline solutions are decolourised, but the yellow colour rapidly returns on exposing the reduced liquid to the air.

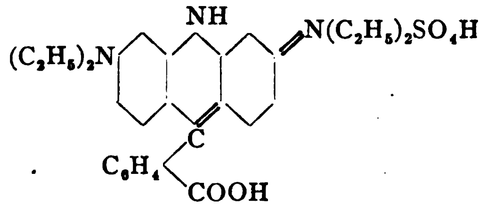
When heated with 3 or 4 parts of hydrochloric acid to 160°–180°, chrysaniline is decomposed with formation of ammonium chloride and chrysophenol, $C_{19}H_{15}N_2O$, in the same way that flavaniline yields flavenol.

Phosphine behaves to fibres like the other basic aniline dyes. It produces a yellow on silk or wool, and is used in admixture with magenta for dyeing silk scarlet. On cotton mordanted with aluminium acetate it gives a nankin-yellow which will stand soaping.

Acids redden fibres dyed with phosphine, and after a time the colouring matter is removed. Alkalies turn the fibre to a greenish-yellow paler than the original. Reducing agents decolourise it gradually.

Flaveosine, the constitution of which has already been mentioned, is obtained by melting *m*-acetaminodimethylaniline with phthalic anhydride. On hydrolysis with concentrated sulphuric acid, acetic acid and ammonia are removed and a salt of flaveosine produced. (See Grandmougin and Lang, *Ber.*, 1909, **42**, 4014.)





Flaveosine is a yellow dyestuff, the free base of which dissolves readily in methyl and ethyl alcohols, acetic acid and acetone, the solutions exhibiting a green fluorescence; it is, however, less soluble in benzene, ethyl acetate, chloroform and carbon tetrachloride and insoluble in ether and light petroleum. Concentrated sulphuric acid gives a bright yellow solution with a blue-green fluorescence; dilution first gives a deep red solution with a faint brown fluorescence and ultimately a yellowish-orange solution with a green fluorescence. The analogy to the rhodamines is evident from the formula; like these compounds it may be esterified, the esters being the analogues of the anisolines.

Corioflavines.—These dyestuffs have been comparatively recently introduced by the Griesheim-Elektron Co. of Frankfurt, a. M., and are used in leather-dyeing and calico-printing. Corioflavine GG is a brown powder, Corioflavine G a red-brown powder; both dyes dissolve in concentrated sulphuric acid with yellow colour and greenish fluorescence; the colour goes to a red-brown on dilution. Corioflavine R forms a brown-red powder which dissolves in concentrated sulphuric acid with greenish fluorescence and orange colour going red on dilution. Corioflavine RR gives a greenish-yellow shade with green fluorescence in concentrated sulphuric acid; the colour goes red on dilution. The corioflavines are insoluble in sodium hydroxide of 52° Tw. (29.7° Be.)

QUINOLINE DYESTUFFS.

Commercial name	Formula	Remarks
Cyanine. . .	(*a*) From methiodides of quinoline and lepidine—$C_{21}H_{19}N_2I$. (*b*). From ethiodides of quinoline and lepidine—$C_{23}H_{23}N_2I$.	By heating alkyl (*e. g.* amyl, etc.) iodides of quinoline and lepidine with alkali.
Flavaniline.	$C_6H_4\left\langle\begin{matrix}C\,(CH_3):C \\ \qquad\qquad\ \vert \\ N \qquad\quad C.(1)C_6H_4(4).NH_2.HCl\end{matrix}\right.$	By heating acetanilide with zinc chloride or condensation of *o*- with *p*-aminoacetophenone.
Flavaniline S.	Sodium salt of flavaniline- Sulphonic acid.	. . . .
Quinoline Red.	Base:—$C_{26}H_{18}N_2$ Hydrochloride:—$C_{26}H_{18}N_2.HCl$	From quinaldine, isoquinoline and benzotrichloride.
Quinoline Yellow, spirit soluble. Quinophthalone.	$C_6H_4\left\langle\begin{matrix}CO \\ C\end{matrix}\right\rangle C{=}CH.C_9H_6N$	Condensation of quinaldine with phthalic anhydride in presence of zinc chloride.
Quinoline Yellow S (water soluble).	Sodium salt of sulphonic acid derivative of quinophthalone.	. . . .
Acridine Orange.	$(CH_3)_2N(4)C_6H_3\left\{\begin{matrix}(2)N\ \ (2) \\ \vert \\ (1)CH(1)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2.HCl+ZnCl_2$	From formaldehyde and dimethyl-*m*-phenylene-diamine.
Acridine Orange R.	$(CH_3)_2N(4)C_6H_3\left\{\begin{matrix}(2)N(2) \\ \vert \\ (1)C\,(1)\end{matrix}\right\}C_6H_3(4)N(CH_3)_2H\,Cl$ $\vert$ C_6H_5	From benzaldehyde.
Acridine Yellow.	$\left.\begin{matrix}CH_3(5) \\ NH_2(4)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(2)N\ \ (2) \\ \vert \\ (1)CH(1)\end{matrix}\right\}C_6H_2\left\{\begin{matrix}(5)CH_3 \\ (4)NH_2.HCl\end{matrix}\right.$	From formaldehyde and *m*-tolylene-diamine.

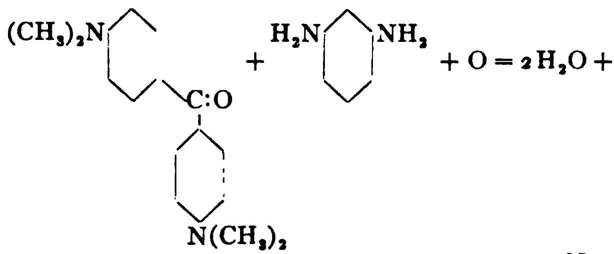
QUINOLINE DYESTUFFS.

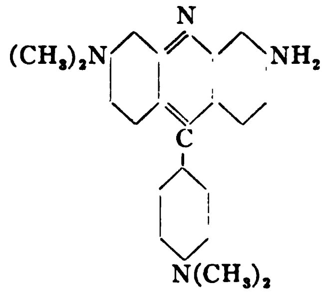
Character of dyestuff	Reaction of aqueous solution: With sodium hydroxide	Reaction of aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Green crystals, blue solution.	Blue ppt.	Colourless.	Colourless.	Colourless.	Too sensitive for use as dyestuffs but employed in sensitising photographic plates.
Orange crystals, blue reflex, yellow solution.	White ppt.	No change until in considerable excess.	Colourless.	....	Obsolete.
Orange powder, yellow solution.	Decolourised	....	Colourless.	Yellow.	Obsolete.
Red crystals, red solution.	....	....	Colourless.	Red.	Very sensitive to light. Colours silk in eosine-shade with strong fluorescence.
Yellow powder, insoluble in water.	....	....	Orange solution.	Yellow ppt.	Crystallised from alcohol; fine yellow needles m. p. 235°. No basic properties.
Yellow powder, yellow solution.	Darker.	Brighter.	Orange.	Yellow.	Dyes wool; application limited on account of price.
Orange powder, orange solution, green fluorescence.	Ppt. (yellow).	Red.	Lighter.	Orange.	Soluble in alcohol.
Orange powder, orange solution, green fluorescence.	Yellow ppt.	Red.	Lighter.	Orange.	Soluble in alcohol.
Yellow powder, yellow solution, green fluorescence.	Pale yellow ppt.	Red with concentrated acid.	Yellow.	....	Soluble in alcohol.

Commercial name	Formula	Remarks
Benzoflavine.	$\left.\begin{matrix}CH_3(5)\\ NH_2(4)\end{matrix}\right\} C_6H_2 \left\{\begin{matrix}(2)N(2)\\ (1)C(1)\end{matrix}\right\} C_6H_2 \left\{\begin{matrix}(5)CH_3\\ (4)NH_2.HCl\end{matrix}\right.$ C_6H_5	From benzaldehyde.
Corioflavine GG. (Griesheim-Elektron).	....	....
Corioflavine G.	....	....
Corioflavine R.	....	....
Corioflavine RR.	....	....
Chrysaniline. Phosphine, etc.	$C_6H_4 \left\{\begin{matrix}(2)N(2)\\ (1)C(1)\end{matrix}\right\} C_6H_3(6)NH_2$ $C_6H_4(4)NH_2$	Bye-product of magenta manufacture.
Flaveosine.	$(CH_3)_2N(4)C_6H_3 \left\{\begin{matrix}(2).NH.(2)\\ (1).C:(1)\end{matrix}\right\} C_6H_3(4):N(CN_3)_2$ $(1)C_6H_4(2).CO—O$	From acetyl-diethyl-*m*-phenylene-diamine and phthalic anhydride.
Rheonine.	$(CH_3)_2N(4)C_6H_3 \left\{\begin{matrix}(2)N(2)\\ (1)C(1)\end{matrix}\right\} C_6H_3(4)NH_2$ $(1)C_6H_4(4)N(CH_3)_2$	By condensation of *m*-phenylene-diamine with Michler's Ketone in presence of zinc chloride.

Character of dyestuff	Reaction or aqueous solution: With sodium hydroxide	Reaction or aqueous solution: With hydrochloric acid	Reaction of dye with sulphuric acid: With conc. acid	Reaction of dye with sulphuric acid: On dilution with water	Other characteristics
Orange powder, yellow solution.	Pale yellow.	Orange.*	Greenish-yellow.	Orange.*	The salts are easily precipitated by the corresponding acids. Decolourised by stannous chloride in hydrochloric acid.
Brown powder.	Insoluble.	....	Yellow solution, greenish fluorescence.	Red-brown.	For leather and calico-printing.
Red-brown powder.	Insoluble.	....	Yellow solution, greenish fluorescence.	Red-brown.	
Brown-red powder.	Insoluble.	....	Orange solution, Greenish fluorescence.	Red.	
Red powder.	Insoluble.	....	Greenish-yellow solution. Green fluorescence.	Red.	
Orange powder, orange solution.	Yellow. ppt.	Brighter.	Orange.	Orange.	Solutions easily give precipitates of sparingly soluble nitrate on addition of nitric acid.
Yellow dyestuff.	Ppt.	....	Bright yellow solution. Blue-green fluorescence.	Successively; deep red solution, faint brown fluorescence; yellow orange solution, green fluorescence.	
Yellow-brown dyestuff.	....	Brown-red.	Yellowish-green.	Original colour.	For cotton, tannin mordant, also leather.

Rheonine is a yellow-brown dyestuff employed on tannin mordants and as a leather dye. It is produced by the Badische Anilin und Sodafabrik (German patent 82, 989) by condensing *m*-phenylenediamine and Michler's ketone at 200° with the aid of zinc chloride.



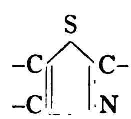


The corresponding hexamethyltriaminophenylacridine has been prepared and examined by Grandmougin and Lang (*Ber.*, 1909, **42**, 3631).

12. THIAZOLE AND SULPHUR DYES.

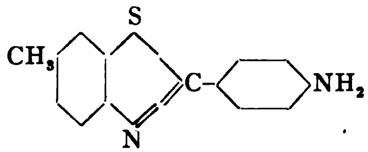
Dyestuffs in which sulphur forms an integral part of the chromophoric groups have already been mentioned in the case of the thiazines, but there still remains a class of substances in which the sulphur is either introduced into the molecule by fusion of suitable aromatic compounds with sulphur, or by heating various substances (not infrequently colouring matters themselves) with an alkaline sulphide.

Thiazoles.—The dyestuffs of the thiazole group contain a 5 membered ring

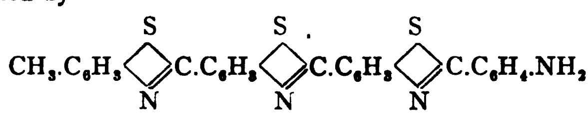


and are commonly prepared by heating together *p*-toluidine or analogous base with sulphur; the simplest thiazole derivatives are colourless and it is only when several nuclei are joined together that actual colouring matters are produced. The first discovered substance of the series is A. W. Hofmann's phenylbenzthiazole produced by melting benzanilide with sulphur; it is technically unimportant.

A. G. Green made the important discovery that *p*-toluidine when heated somewhat strongly with sulphur yielded a coloured base; the initial product is *dehydrothio-p-toluidine;* while if the heating be prolonged, another substance of more intense colour and slighter solubility and basicity is produced which has received the name of Primuline. The constitution of dehydrothiotoluidine was established as



while in the case of primuline further consideration of the dehydrothioparatoluidine has occurred and very possibly the base contains 3 thiazole rings in the molecule. If so, its constitution may be represented by



(Green, *Ber.*, 1889, **22**, 969; Gattermann, *Ibid.*, 424, 1064; Jacobson, *Ibid.*, 331; Anschütz and Schultz, *Ibid.*, 581).

Primuline base evidently contains a free amino-group, as it is readily diazotised; it may also be sulphonated and is usually employed in this form.

Primuline is obtained by heating 2 molecules of *p*-toludine with 4 to 5 equivalents of sulphur at 200° to 280°; the primuline base so obtained is then treated with fuming sulphuric acid. The commercial product is a yellow powder, which is very soluble in hot water. The very dilute aqueous solution of Primuline exhibits a blue fluorescence. In a 5% neutral bath at a boiling temperature, Primuline dyes cotton a lemon-yellow colour, which is tolerably fast to scouring, entirely unaffected by alkalies, and turned a golden yellow by acids. The affinity of the fibre for the colouring matter is increased, and con-

sequently deeper shades may be obtained, by addition of sodium chloride or sulphate to the bath. Reducing agents produce no change, but the colour is attacked by oxidising agents, such as bleaching powder or chromic acid. By the latter the shade is changed to olive, while boiling solutions of hypochlorites turn the colour to orange-yellow, which is very fast to all agents.

The aqueous solution of the dyestuff is unaffected by the addition of sodium hydroxide, while hydrochloric acid throws down a yellow precipitate. The dyestuff dissolves in strong sulphuric acid to a pale yellow solution with a green fluorescence; dilution with water causes the separation of an orange-yellow precipitate.

Since Primuline contains an amino-group, it is capable of being diazotised, and this operation may be readily performed on the dyed fibre by passing the washed material through a dilute solution of sodium nitrite (3 to 5%) acidified with sulphuric acid. If the fabric be then again washed and immersed without delay in a developing solution of one of the naphthols, naphthylamines, or their derivatives, various shades of yellow, orange, scarlet, or maroon may be obtained. The colours so obtained are termed *ingrain colours*, and are characterised by their extraordinary fastness to scouring, milling, acids, etc., being said to be only equalled in this respect by alizarin and its congeners, and to far exceed the ordinary benzidine dyes.

Chloramine Yellow is a dyestuff of unknown constitution, obtained by the oxidation of dehydrothiotoluidine-sulphonic acid. It is a brownish-yellow powder, soluble in water with a yellow colour, but insoluble in alcohol. The addition of either hydrochloric acid or sodium hydroxide to the solution produces an orange-yellow precipitate. With strong sulphuric acid the dyestuff yields a deep red solution from which a light brown precipitate is thrown out on dilution with water. Chloramine Yellow produces pure yellow shades on wool and unmordanted cotton, which are fast to light.

Oxyphenine, Oxyphenine Gold, Chlorophenine G and Thiophosphine J are dyestuffs which are produced in a manner similar to the above, and no doubt possess an analogous constitution. Their properties and application are the same as chloramine yellow.

Mimosa is a diazotised compound of primuline, treated with ammonia. Its formula and constitution have not been determined. It is sold in the form of a yellowish-brown powder, soluble in water and alcohol with a yellow colour. With hydrochloric acid the aqueous

solution throws down an orange precipitate, while sodium hydroxide gives a scarlet precipitate. Strong sulphuric acid gives a yellowish-brown solution, which on dilution with water yields a brown precipitate and evolves nitrogen. Mimosa dyes a yellow on unmordanted cotton which is fast to soap but fugitive to light.

Chromine G is a dyestuff similar to Thioflavine S, and is obtained by the action of sulphur at elevated temperatures on dehydrothiotoluidine, methylating the product so obtained, and then sulphonating by means of fuming sulphuric acid. It is a yellowish-brown powder, giving a yellow solution in water and alcohol. The aqueous solution treated with hydrochloric acid suffers scarcely any change, a slight brownish precipitate being formed. Sodium hydroxide turns the solution to a greenish-yellow. Strong sulphuric acid dissolves the dyestuff to a greenish-yellow solution, exhibiting a blue fluorescence and giving an orange precipitate on dilution with water. Chromine G is employed in the same manner as Thioflavine S, yielding fine yellow shades which are fast to soap but very fugitive to light.

Thioflavine T, $C_{17}H_{19}N_2SCl$, is the trimethyl chloride derivative of dehydro-thiotoluidine, and has the following constitution:

$$CH_3.(4)C_6H_3\left\{\begin{matrix}(2).S:\\(1).N:\end{matrix}\right\}C.(1)C_6H_4(4).N(CH_3)_3Cl$$

It is obtained by the action of methyl chloride on dehydrothiotoluidine or by the action of methyl alcohol and hydrochloric acid. It is brought into commerce in the form of a yellow crystalline powder which is easily soluble in water and alcohol with a yellow colour, the solutions possessing a green fluorescence, especially the alcoholic solution. The aqueous solution is unaffected by the addition of sodium hydroxide or by hydrochloric acid. With strong sulphuric acid the dyestuff gives a colourless solution which becomes yellow on dilution with water. Thioflavine T is used for dyeing silk and cotton mordanted with tannin; the shades so obtained are a fine greenish-yellow which on silk exhibit a green fluorescence. In addition to Thioflavine T, Messrs. Cassella and Co. have introduced another mark, Thioflavine TCN.

Thioflavine S is a yellow dyestuff of acid properties which results from the methylation of dehydrothio-*p*-toluidine-sulphonic acid. The dyestuff is a sulphonic acid salt which is sold in the form of a yellow powder, soluble in water and alcohol with a yellow colour, the solution in the latter possessing a green fluorescence. The addition of sodium

hydroxide causes no change in the aqueous solution, but hydrochloric acid throws down an orange-yellow precipitate. The dyestuff dissolves in strong sulphuric acid to a brownish-yellow solution from which an orange precipitate separates on dilution with water. Thioflavine S dyes unmordanted cotton from an alkaline bath, but the shades produced are not fast to light or acids, though they resist alkalies fairly well. They are unaffected by reducing agents and cannot be stripped from the fibre.

Clayton Yellow (*Thiazole Yellow S*).—While dehydrothiotoluidine and its sulphonic acid may be diazotised and coupled with naphthols, etc., it is also capable of combining with diazotised bases, though possibly the substances formed in this way are diazo-amino-compounds as they are not capable of further diazotisation. Clayton Yellow comes in this class; it is produced by the combination of diazotised dehydrothiotoluidine-sulphonic acid with the non-diazotised acid. It dyes unmordanted cotton a fine yellow from an alkaline bath.

Erica is obtained by the diazotisation of dehydrothio-*m*-xylidine and coupling with α-naphtholdisulphonic acid-ϵ. It is a red dyestuff used on unmordanted cotton. It gives a violet colour with concentrated sulphuric acid and is slowly decolourised by stannous chloride in hydrochloric acid solution.

Sulphur Dyes.—The first dyestuffs of this class were discovered in 1873 by Croissant and Bretonnière who produced them by heating a variety of organic substances either with alkaline sulphides or a mixture of sulphur and sodium hydroxide; among the materials used, sawdust, bran, straw and excrement may be mentioned.

Cachou de Laval, as the resulting dyestuff was called, received considerable application despite its unpleasant smell. It is soluble in water, but is precipitated on prolonged boiling. It appears to behave like a reduced colouring matter which is developed by means of oxidation. It yields brown and greyish-brown colours on cotton, which serve as a bottom shade and mordant for other adjective dyestuffs. The shades obtained are quite fast to light and exceedingly fast to soap. On the addition of acids to the dyestuff, hydrogen sulphide is liberated, and the colouring matter together with sulphur is precipitated. *Cachou de Laval S* is the dyestuff purified from excess of alkaline sulphide. It is used in calico-printing.

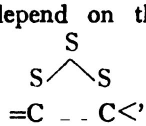
After this, practically no progress was made for almost 20 years, when Vidal discovered that useful black dyestuffs might be produced

by the action of sodium sulphide and sulphur on *p*-aminophenol and *p*-phenylenediamine. This was followed by patents on all sides, aromatic compounds alone being employed; and with regard to the production of *Cachou de Laval*, it is worth noting that Wichelhaus (*Ber.*, 1907, **40**, 126) draws attention to the observation of Cross and Bevan (Cellulose, *ed.* 1903, p. 68) that cellulose gives rise to phenols on heating, so that even Cachou de Laval may well possess an aromatic structure.

The manner in which the sulphur is combined in these compounds is not quite certain; very possibly in the *Immedial Yellow* group some, at least, of the sulphur is present in a thiazole ring, especially considering the fact that the dyes of this class are prepared by the action at a fairly high temperature of sulphur on *m*-diamines in which an alkyl group is situated in the ortho-position to one of the amino-groups.

In the case of the *Immedial Pure Blue* dyes it is possible that a thiazine ring is produced, but in any case there seems to be a concensus of opinion that in the sulphur dyes 2 or more molecules of a simple character are linked together by a disulphide grouping (-S-S-) and that when dissolved in alkaline sulphides, some at least of these linkages are split with formation of -SNa groups. In fact, one of the most characteristic properties of the sulphur dyes is the way in which they dissolve more or less easily in sodium sulphide, from which solutions they may be reprecipitated either by acids or air-blowing. Nietzki considers it probable that they are contained in the alkaline sulphide solutions in the form of leuco-compounds. So far, the dyestuffs as separated by the action of air or carbon dioxide have not been obtained in a crystalline condition.

Another view as to the manner in which sulphur is contained in these dyestuffs has been advanced by H. Erdmann (*Annalen*, 1908, **362**, 133–178) who considers the reactivity of molten sulphur to depend on the existence of "thiozone," S_3, molecules. A ring,



, is supposed to be produced which apparently possesses chromophoric and substantive properties.

Nietzki (*Organische Farbstoffe*, 1906, p. 292) divides the sulphur dyes into 6 groups; the classification is perhaps somewhat provisional but nevertheless useful.

1. Immedial Yellow Group.

These dyes are produced from *m*-diamines containing a side chain (especially *m*-tolylene-diamine 1 : 2 : 4), various formyl- and acetyl-derivatives and also nitroformyl- and nitroacetyl-compounds. On fusing these with sulphur at fairly high temperatures, difficultly soluble compounds are produced which are, however, rendered soluble by heating with concentrated solutions of sodium sulphide. Acids precipitate the dyestuffs from these solutions, but they are now in condition to dissolve easily in dilute solutions of sodium sulphide, and may be fixed on cotton as substantive dyes.

From the method of preparation it might appear probable that the the dyestuffs of this class are amino-derivatives of dehydrothio-toluidine seeing that *m*-tolylenediamine is the monoamino-derivative of *p*-toluidine, but any assumption of this sort has to be made with caution as possibly the sulphur to a certain extent displaces nitrogen and during the fusion ammonia is evolved.

Pyrogene Yellow M (the first yellow dyestuff of the group) and *Pyrogene Olive N* are protected by the German patent 135,335 of the Gesellschaft für chemische Industrie in Basel which describes processes for heating various methylamino-, nitroamino-compounds, etc., with sulphur and alkaline sulphides or alkalies.

Cassella's Immedial Yellow D is obtained from *m*-tolylene-diamine and sulphur at 190°, while at 250° *Immedial Orange* is produced from the same materials. *Eclipse Yellow* (Geigy) from diformyl-*m*-tolylenediamine and sulphur at 240°, and *Thion Yellow* (Kalle & Co.) obtained by heating thio-*m*-tolylenediamine with sodium sulphide solution, belong to the same group.

Other yellow sulphur dyes are *Thioxine Yellow G* and *Thioxine Orange* of the *Chemische Fabrik Griesheim-Elektron.* The former, a yellow-brown powder, dissolves slightly in concentrated sulphuric acid with yellow colour giving an orange precipitate on dilution while it is insoluble in sodium hydroxide. The latter is a reddish-brown powder, slightly soluble in sulphuric acid and insoluble in sodium hydroxide.

Eclipse brown is obtained by heating *m*-tolylenediamine and oxalic acid with polysulphides.

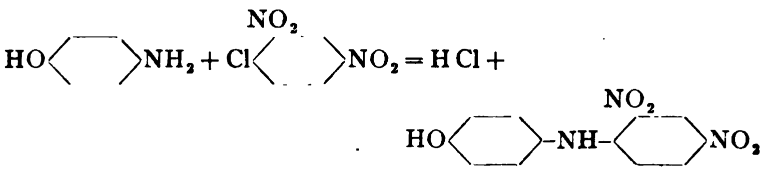
2. Vidal Black Group.

Vidal claimed the fusion of a large number of organic compounds with polysulphides for the preparation of dyestuffs, but apparently

only *p*-aminophenol and dinitrophenol were applied in practice. The black from *p*-aminophenol was soon displaced by *Immedial Black;* on the other hand the black from dinitrophenol has proved a very valuable dye. *Vidal Black for Cotton* gives a greenish-black solution with concentrated sulphuric acid; it undergoes little alteration with concentrated hydrochloric acid and is unaffected by the dilute acids. With nitric acid (sp. gr. 1.40) it fades to a grey, fades to bluish-green with sodium hydroxide (10%) and goes a dirty yellowish-brown with stannous chloride and hydrochloric acid. *Vidal Black S for Cotton* gives blue black and violet reactions with concentrated sulphuric and nitric acids respectively; its other reactions are similar to those already given.

3. Immedial Black Group.

The dyestuffs of this class are obtained by sulphurising derivatives of diphenylamine, *Immedial Black* being produced from *p*-hydroxy-*o'*-*p'*-dinitrodiphenylamine, a compound which results from the condensation of *p*-aminophenol with dinitrochlorobenzene



If during the process of sulphurising the temperature be kept low, *Immedial Blue* (not to be confused with the Immedial Pure Blue from *p*-dimethylamino-*p'*-hydroxydiphenylamine) results.

Immedial Black V, the product from hydroxydinitrodiphenylamine, gives a bluish-grey with concentrated sulphuric acid, but undergoes little or no alteration with dilute acid or hydrochloric acid. Nitric acid (sp. gr. 1.40) gives a bordeaux-red; dilute alkalies have little action and it is decolourised by stannous chloride and hydrochloric acid.

Immedial Black N, obtained by the action of polysulphides on dinitrophenol is but slightly affected by the reagents mentioned.

Sulphur Black T extra (A. G. für Anilin Fabrikation, Berlin) is obtained from dinitrophenol and polysulphides in dilute aqueous solution, while by careful fusion of the same materials the Gesellschaft für Chemische Industrie in Basel obtain *Thiophenol Black T extra.* This, like the *Pyrogene Black* of the same firm, gives a violet-black

solution in concentrated sulphuric acid but practically no other reactions with acids and alkalies.

The Thioxine Blacks (GBOOO, 3BOOO, RTOOO) of the Chemische Fabrik Griesheim-Elektron, form black powders used for cotton. They are insoluble in concentrated sulphuric acid, sparingly soluble in sodium hydroxide (52° Tw.) with a blue colour.

Auronal Black (Weiler ter Meer) probably belongs to the same class, being produced by sulphurising *p*-aminodinitro-diphenylamine in presence of glycerin. It is a direct cotton dye which gives a blackish-green solution in concentrated sulphuric acid.

As mentioned above, a lower temperautre during the process of sulphurising leads to the production of blue dyestuffs from hydroxydinitrodiphenylamine.

Immedial Blue C (Cassella) gives a green colour with nitric acid (sp. gr. 1.40); various marks (C, C extra conc. CB, CR, etc.) are sold. It is but little affected by other reagents.

The Pyrogene Blues and Greys are produced by heating hydroxydinitrodiphenylamine and indophenols under pressure with polysulphides in alcoholic solution. *Pyrogene Blue RR* gives a violet-black solution with concentrated sulphuric acid and turns reddish with nitric acid (sp. gr. 1.40).

Immedial Indone, obtained from the Indophenol produced by oxidising *o*-toluidine with *p*-aminophenol, is placed on the market in various marks. Mark R gives a deep blue solution in concentrated sulphuric acid, bluish-violet on dilution; it turns redder with nitric acid.

Pyrogene Indigo is obtained by heating the indophenol $C_6H_5.NH.$-C_6H_4.-N : C_6H_4: O with polysulphides.

4. Immedial Pure Blue Group.

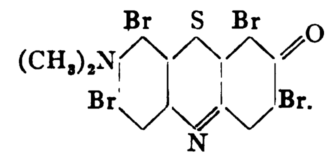
The colouring matters of this group are closely related to the thiazines (Methylene Blue, etc.). The Gesellschaft für Chemische Industrie in Basel found that beautiful blue dyes resulted by heating the indophenol

$$(CH_3)_2N.C_6H_4.N:C_6H_4:O$$

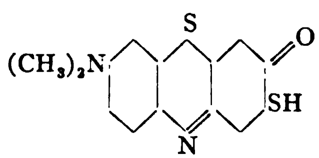
with polysulphides, and Cassella & Co. discovered that by keeping a low temperature and in presence of a considerable amount of water a pure blue dyestuff (*Immedial Pure Blue* or *Pyrogene Blue*) was obtained.

The colouring matters of this group differ from the Immedial Blacks by containing 1 nitrogen atom less.

These dyes belong to the Thiazine Series, as shown by the researches of R. Gnehm and F. Kaufler (*Ber.*, 1904, **37**, 2617, 3032). Immedial Pure Blue was obtained according to the directions of German patent 134,947 by fusing *p*-dimethylamino-*p*′-hydroxydiphenylamine with sulphur and purified by means of the hydrochloride of the leuco-compound. Bromination, effected by heating to 115–125 with hydro-bromic acid and potassium bromate, gave a substance $C_{14}H_8ON_2SBr_4$ identical with that obtained from Bernthsen's Methylene Violet, hence there is little doubt that its constitution must be expressed by the structural formula



This result, combined with the fact that a sulphur dye having the properties of Immedial Pure Blue results by the oxidation of dimethyl-*p*-phenylenediamine-thiosulphonic acid in presence of *o*-thiophenol or the corresponding dihydroxydiphenyl disulphide in alkaline solution, make it very probable that the actual Immedial Pure Blue colouring matter is the disulphide corresponding to the mercaptan



A. Bernthsen (*Chem. Zeit.*, 1908, **32**, 956) confirms the formation of blue sulphide dyestuffs when Methylene Violet is heated with sodium sulphide, but draws attention to the lack of proof that the Methylene violet nucleus remains intact.

Immedial Pure Blue gives a bluish-violet solution in concentrated sulphuric acid going to blue on dilution, nitric acid (sp. gr. 1.3) a violet colour; on the fibre it is immediately decolourised (pale yellow) by stannous chloride and hydrochloric acid.

5. Phenazine Derivatives.

A large number of dyes have been obtained by the action of alkaline sulphides and sulphur on aminohydroxyphenazines (Safraninone) and allied compounds. These substances almost certainly contain the original azine ring intact, the result of sulphurising being the introduction of mercaptan groups (readily oxidisable to disulphides). Among dyestuffs of this class the *Thiogene Purple* and *Thiogene Dark Red* (G and R-) of Meister, Lucius and Brüning, the *Immedial Bordeaux* (*G* and *GF*) and *Immedial Maroon B* of Cassella, Bayer's *Catigene Red-brown* and Geigy's *Eclipse Red* may be mentioned.

6. Dyestuffs From 1:5-and 1:8-Dinitronaphthalene.

One of the most important dyes of this group is the *Fast Black B* of the Badische Co., obtained by heating dinitranaphthalene with sodium sulphide in aqueous solution. It is worth noting that about 30 years ago Rudolf Böttger observed the production of a violet cotton dye by treating dinitronaphthalene with sodium sulphide, while fast black may also be obtained from the intermediate products of the preparation of naphthazarine and from various naphthaquinoneimides. *Melanogene Blue* (Meister, Lucius and Brüning) which is obtained from 1:5-dinitronaphthalene and alkaline polysulphides must also be mentioned here.

Reference must be made also to the sulphur greens which result from the fusion of various indophenols with polysulphides in presence of copper compounds; the Gesellschaft für Chemische Industrie in Basel prepares *Pyrogene Green* (*B*, *FB*, *FF*, *2G*, *3G*) and *Pyrogene Dark Green B* by sulphurising *p*-aminophenol and its substitution derivatives with sodium sulphide and sulphur in presence of copper.

Further, a number of dyestuffs in addition to Cachou de Laval, are obtained by sulphurising saw-dust, bran, etc.; one may mention *Pyrogene Brown D*, *Catigene Black Brown N*, *Cryogene Brown*, *Cattu italiano*, etc.

Cryogene Brown gives a dirty brown with concentrated sulphuric acid and nitric acid (sp. gr. 1.40), it is unaltered by 10% sodium hydroxide and changes to a light brown with stannous chloride and hydrochloric acid.

With regard to the names used for the sulphur dyestuffs, it has

probably been noted that the same prefix frequently occurs and that this relates, not to the materials from which the dyestuff is produced, but to the firm by which it is manufactured. Appended is a short list of these prefixes:

Catigene	Bayer & Co. (Elberfeld).
Clayton	Clayton Aniline Co. (Manchester).
Cryogene..........	Badische Anilin- und Soda-Fabrik.
Eclipse	Geigy (Basel).
Immedial	L. Cassella & Co. (Frankfurt).
Melanogene	Meister, Lucius & Brüning (Höchst a/M).
Pyrogene..........	Gesellschaft für Chemische Industrie (Basel).
Thiogene..........	Meister, Lucius & Brüning.
Thion.............	Kalle & Co. (Biebrich).
Thiophor..........	Jäger.
Thioxine..........	Chemische Fabrik Griesheim-Elektron (Frankfurt).

COLOURING MATTERS OF NATURAL ORIGIN.

By PROF. W. M. GARDNER, M. Sc.

The colouring principles from which natural colouring may be derived are very widely distributed in the vegetable kingdom. Natural colouring matters have been used by the natives of countries to which they are indigenous from very early times. Very few important natural dyes, however, are native to Europe, but a considerable number were imported in large quantities from the tropics prior to the introduction of the coal-tar dyes. Although the natural dyes have been to a great extent replaced by coal-tar derivatives, the use of certain natural products is still very prevalent, those now chiefly employed being indigo, logwood, and fustic, but a number of others still find considerable application for special purposes, and among these may be mentioned cochineal, orchil, madder, catechu, and turmeric.

Some natural dyestuffs, for example cochineal, are used without any previous preparation. In other cases the natural product undergoes a certain preliminary treatment, as in the "ageing" of logwood; while the preparation of commercial indigo involves a more complex treatment of the product formed by natural processes.

The colouring matter present in a natural dye is usually associated in the commercial product with a considerable amount of organic extractive matter, inert vegetable matter, mineral matter, etc. An exact estimation of these products is thus frequently a matter of great difficulty, and since the secondary substances usually have an influence, adverse or otherwise, on the use of the dyestuff, a small scale experiment in dyeing or printing, carried out as far as practicable under the conditions in which the material will be used in practice, is very often the most satisfactory means of estimating the commercial value of a natural dyestuff. Special methods are, however, available in certain cases, and such will be described under their proper headings.

INDIGO.

Indigo has long been regarded as the most valuable and important of all dyestuffs. Certain species of indigo plant are found in most tropical countries, and have been used by the natives of these countries as dyes or stains from time immemorial. The largest amount of indigo is produced in the Indian provinces of Bengal, Oudh, and Madras, but it is also cultivated in China, Japan, Java, Manilla, Central America, Brazil, and certain parts of Africa. Each of these countries exports its own special commercial brands, which are distinguishable by experienced buyers by reason of their physical properties.

The indigo-yielding plants do not all belong to the same botanical family, but the most important commercial varieties are all species of the genus *Indigofera*. *I. Sumatrana* is the species chiefly cultivated in India, though it is now being replaced by the Javanese plant *I. Arrecta*, from which a better yield is obtained.

The *Isatis Tinctoria* or woad plant is the European indigo plant, but is not now cultivated as a source of the dye, although it is still grown in England and Belgium, and, after preparation, used in the woad indigo vat to assist fermentation.

Preparation of Indigo.

The indigo plant is grown from seed each year, being cut down when the flowers begin to open, fresh shoots springing from the roots. The indigo-producing substance resides principally in the leaves.

Indigotin, the real colouring matter, does not exist in the plant, but is produced by the decomposition of a glucoside, *indican*, $C_{14}H_{17}O_6N$. A method of preparing this substance from the plant in quantity has recently been described. (A. G. Perkin and W. P. Bloxam, *Trans.*, 1907, **91**, 1715).

To obtain indigo from the plant, the freshly cut plants are extracted with water in "steeping vats." Fermentation ensues, and the extracted indican is decomposed by a specific enzyme present in the plant. The liquid is then run into "beating vats" where it is agitated, and atmospheric oxidation changes the yellow colour of the liquid to green, and finally the indigo separates in flakes. The indigo pulp is collected and boiled with water to prevent secondary fermentation, and is finally pressed into cakes and dried at a low temperature.

The quality and yield of indigo obtained depend greatly not only on the quality of the plant, but also on the skill brought to bear in the manufacturing process, and latterly by increased attention to these as well as to selection of seed, manuring of crops, etc., much better yields have been obtained.

Associated with the blue colouring matter there is usually from 1 to 5% of a red colouring matter, *Indirubin*, which is also produced by the decomposition of indican. The amount of this red dye is increased by the addition of alkali to the steeping vats. Indican is a glucoside, and produces dextrose on decomposition, some brown amorphous product is also invariably formed.

Rawson states that the average amount of indigo produced from 100 pounds of fresh plant is about 4 ounces.

The glucoside, indican, $C_{14}H_{17}O_6N$, was first isolated by Schunck in 1850. It is a pale-coloured amorphous substance, soluble in water, alcohol, and ether. It has a bitter taste, and a slight acid reaction. It crystallises from water with $3H_2O$ and in this condition its m. p. is 57–58°. When heated to 100°, it becomes anhydrous. It melts at 176–178°.

Indican has been shown by Hazewinkel (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 512) to be a glucoside of indoxyl, the sugar obtained from it being dextrose. The normal decomposition of indican results in the formation of indigotin by oxidation of indoxyl, but by combination of the latter with isatin, indirubin is formed.

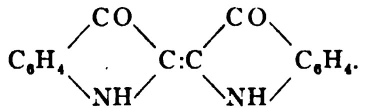
Another secondary change results in formation of the brown amorphous products by the condensation of indoxyl. The main brown product of this condensation has been named by Perkin (*Trans.*, 1907, **91**, 1728) *indoxyl brown* and has a percentage composition almost identical with that of the main constituent of indigo brown, which it closely resembles.

A substance allied to indican occurs under certain conditions in urine and gives rise to a blue colouration owing to the formation of indigotin.

The amount of indican in the leaves of the indigo plant may be estimated by decomposing the glucoside extracted from the leaves, by sulphuric acid and combining the indoxyl thus formed with isatin to form indirubin (*Trans.*, 1907, **91**, 4) or by oxidising the indoxyl to indigotin by means of ammonium persulphate (*Trans.*, 1907, **91**, 1728).

Constituents of Indigo.

Indigotin, $C_{16}H_{10}O_2N_2$, has the constitution



It is the true colouring matter of indigo, from which it may be prepared in a variety of ways, but for analytical purposes it is best prepared from synthetic indigo, such as Indigo Pure, (B. A. S. F.). This product is boiled with a 10% solution of pure sulphuric acid several times, then well washed with water. It is now reduced with sodium hydrosulphite in the presence of sodium hydroxide, the solution filtered, and the indigotin re-oxidised by a current of air. The precipitate is collected, washed with dilute hydrochloric acid, then with alcohol, and dried. It is finally recrystallised from boiling glacial acetic acid, the crystals being washed with alcohol, ether, dilute hydrochloric acid, and lastly with water, and then dried at 105°.

An equally pure product may be obtained according to Gaunt, Thomas, and Bloxam (*J. Soc. Chem. Ind.*, 1907, **26**, 1174) by sublimation. A Jena flask containing the indigo is heated to a temperature of 420° in a bath of fusible metal, a high vacuum being maintained in the flask. The crystals of sublimed indigotin which collect in the upper portion of the flask are finally purified by recrystallising from glacial acetic acid as above described.

Pure indigotin forms dark blue or purple needles which exhibit a coppery lustre. When powdered it possesses a deep blue colour and assumes a bronzy lustre when rubbed. Its sp. gr. is 1.35. When heated, it sublimes at about 290°, the vapour possessing a beautiful red-violet colour, but in the presence of air considerable decomposition occurs. In an inert gas it volatilises unchanged. When submitted to dry distillation it decomposes; yielding aniline as chief product.

Indigotin is a neutral substance and is quite stable at ordinary temperatures; it has neither taste nor smell, and is insoluble in water, cold alcohol, ether, dilute acids, and alkalies, and fatty oils. It is slightly soluble in boiling alcohol with a blue colour, but is again deposited on cooling. It is also slightly soluble in phenol, carbon disulphide, or chloroform, but the best solvents are glacial acetic acid, nitrobenzene,

quinoline, and aniline. The addition of 1 or 2 drops of sulphuric acid greatly increases the solvent action of glacial acetic acid, and from this solution the indigotin may be reprecipitated on dilution with water. Boiling paraffin dissolves indigotin with a magenta colour.

Concentrated sulphuric acid completely dissolves indigotin, sulphonation occurring. The product formed is either the mono-, di-, tri-, or tetra-sulphonic acid, according to the conditions.

When subjected to the action of oxidising agents such as dilute nitric acid, chromic acid, etc., in the presence of water, indigotin is converted into *isatin* ($C_8H_5NO_2$). With hot nitric acid it forms nitrosalicylic acid, $C_6H_3(OH)(NO_2)COOH$, or picric acid, $C_6H_2(OH)(NO_2)_3$, according to the conditions. Further oxidation products, such as oxalic acid and carbondioxide are also formed.

If indigotin is heated with reducing agents in the presence of alkali hydroxide, it is reduced to *indigo white* ($C_{16}H_{12}N_2O_2$), but if the heating be long continued secondary changes take place with the production of a dark red substance, $C_{32}H_{22}N_4O_4$, allied to *flavindine* ($C_{32}H_{24}N_4O_5$) (Giraud, *Bull. Soc. Chim.*, 1880, **34**, 530).

Indigo White, or Reduced Indigo ($C_{16}H_{12}N_2O_2$).—This substance, produced by the action of reducing agents on indigotin, is a greyish-white, amorphous, tasteless, and odourless substance. It is insoluble in water or dilute acids, but is soluble in alcohol, ether, and alkaline solutions, with a yellow colour. On exposure to air its solutions absorb oxygen, becoming at first green, and finally blue, with reproduction and separation of indigotin. Alkaline solutions of indigo white give white precipitates with salts of alumina, zinc, magnesia, or lead, and with stannous, ferrous, and manganous salts. It forms two compounds with lime, one soluble, the other insoluble in water.

The use of indigo in dyeing by the vat method is based upon the production of an alkaline solution of indigo white, with which the material is saturated, the indigo blue being then reproduced on the fibre by air oxidation.

Indigotin Sulphonic Acids.—The monosulphonic acid, $C_{16}H_9N_2O_2(SO_3H)$, also known as *sulphopurpuric acid*, is obtained by mixing 1 part of indigotin with 4 parts of concentrated sulphuric acid, and allowing the mixture to stand for half an hour. On diluting with water a fine purplish-blue precipitate is formed, which is slightly

soluble in water. The sodium salt which also is slightly soluble in water has been used in dyeing under the name of "indigo purple," or "red indigo carmine."

Indigotin disulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, also known as *sulphindigotic acid*, is produced by the further action of sulphuric acid, 1 part of indigotin being heated to 90° for half an hour with 10 to 12 parts of concentrated sulphuric acid. On diluting with water any monosulphonic acid present is precipitated. The disulphonic acid may be purified by adding a saturated solution of common salt, which causes a precipitate of sodium disulphindigotate. It forms an insoluble lead compound, from which the free acid may be separated by hydrogen sulphide. It is easily soluble in water, and (like the monosulphonic acid) is rapidly destroyed by oxidising agents or converted into a leuco-compound by reducing agents. When treated with strong sodium hydroxide or ammonia, it produces first green, and then yellow substances, of which little is known.

Sulphindigotic acid is largely used in dyeing in the form of its sodium salt, which is known as "indigo carmine," or "indigo extract." It is sold as a bronze-blue powder or as a paste. Indigo extracts are estimated by dyeing trials or by titration with permanganate (see page 396).

Indigotin tri- and tetrasulphonic acids are produced by the action of fuming sulphuric acid on indigotin, the latter being formed by heating indigotin with fuming sulphuric acid (25% SO_3) for 20 minutes at 96–98° (W. P. Bloxam, *J. Soc. Chem. Ind.*, 1906, **25**, 736).

Both the di- and tetra-sulphonic acids are made use of in purifying commercial indigos for analysis.

Indirubin or Indigo Red, $C_{16}H_{10}N_2O_2$.—This substance, which is isomeric with indigotin, is produced in small amount in the ordinary process of manufacturing indigo. Like indigotin it is formed from indican, a portion of the indoxyl produced by the hydrolysis being oxidised to isatin which then combines with indoxyl to produce indirubin, this change being facilitated by the presence of alkali. When pure, indirubin forms brownish-red needles, which sublime at 140°. Like indigotin it is insoluble in water, alkali, or dilute acids, but is much more soluble in alcohol than indigo blue, and is also somewhat readily soluble in (commercial) acetone or in pyridine. Concentrated sulphuric acid converts it into a disulphonic acid. Toward reducing agents it behaves similarly to indigo blue, being con-

verted into a compound analogous to indigo white, which is re-oxidised when exposed to the air. It is much less susceptible to the action of oxidising agents than indigotin, and when a mixture of the sulphonic acids is titrated with potassium permanganate, the whole of the indigotin disulphonic acid is destroyed before the indirubin disulphonic acid is attacked. For the same reason, commercial indigo containing indigo red is unsuitable for producing white discharge patterns.

Indirubin produces crimson shades in dyeing by the vat method, but if the vat contains an excess of alkali the indirubin white compound undergoes an intermolecular change and is slowly converted into indigotin white, which on oxidation produces indigo blue.

Indirubin sulphonic acid dyes wool a crimson shade, which is much faster to light than the ordinary indigo-extract dyes.

Indigo Brown.—Brown substances are always present in commercial indigo. They were named by Schunck, ***indiretin*** and ***indihumin***, and are formed by secondary decomposition of indican. The brown matter is soluble in sodium hydroxide solution and in concentrated sulphuric acid.

Rawson states that the longer the liquid is allowed to stand after extraction from the plants before oxidising, the greater the amount of brown produced at the expense of indigo blue (*J. Soc. Chem. Ind.*, 1907, **26**, 279). Perkin and Bloxam (*Trans.*, 1907, **91**, 281) have analysed indigo brown and have obtained figures corresponding with the formula $C_{16}H_{12}O_3N_2$. They found pyridine to be practically its only solvent, and considered that indigo brown is derived by the condensation of indoxyl produced from indican in the steeping vats.

Indigo Yellow.—This substance is frequently present in commercial indigo, particularly Java indigo (Rawson, *J. Soc. Chem. Ind.*, 1899, **18**, 251). It is almost insoluble in water or in dilute acids, but is soluble in concentrated sulphuric acid or in glacial acetic acid. It is easily soluble in alkalies from which solutions dilute acids throw down a pale yellow precipitate. It is soluble in alcohol and ether. It sublimes at a low temperature with much decomposition; it dyes wool mordanted with potassium dichromate a yellow shade resembling that given by weld. It does not dye in the vat.

A. G. Perkin (*J. Soc. Chem. Ind.*, 1907, **26**, 435) has shown that this substance is identical with *kœmpferol*, $C_{15}H_{10}O_6$. Indigo yellow is liable to cause errors in indigo estimations unless previously eliminated.

Synthetic Indigo.—The synthesis of indigo was first completed by Baeyer in 1878, *o*-aminophenylacetic acid being converted into indoxyl, from which isatin was formed. The conversion of this substance into indigotin had been previously achieved by Baeyer and Emmerling in 1870.

Somewhat later Baeyer prepared indigotin from cinnamic acid, and in 1882, in conjunction with Drewsen, he published a new synthesis, in which indigotin was obtained from *o*-nitrobenzaldehyde by treatment with acetic aldehyde in the presence of alkali hydroxide.

In 1893 Kalle & Co. put on the market a product named "indigo salt," which is the sodium bisulphite compound of *o*-nitrophenyllactone. This was used to a limited extent in calico-printing.

In 1890 Heumann's synthesis from phenylglycocol was published, and this was gradually developed into a commercially successful process by the Badische Anilin und Soda Fabrik, who placed their product, "Indigo Pure" on the market in 1897.

This firm, and others now manufacture synthetic indigo on an enormous scale.

Indirubin has also been produced synthetically, and has been put on the market both as an independent product and admixed with indigotin as in natural indigo. It is not much employed.

A very interesting account of the history of the development of the manufacture of synthetic indigo was published in the *Berichte* by Dr. Brunck in October, 1900 (*J. Soc. Dyers and Colourists*, 1901, **17**, 157).

Synthetic indigo is placed on the market as a blue powder of about 98% purity and as a paste containing 20% of indigotin. The chemical and dyeing properties of the product are identical with those of natural indigo.

Commercial Varieties of Indigo.

Natural indigo is sold in a large number of well distinguished commercial varieties, which differ widely in appearance, character, amount of impurities, percentage of colouring matter, proportion of indigo red, etc. The varieties are distinguished by names indicating their origin. For example: Bengal, Java, Guatemala, Caracas, Madras, Manilla, Oudh, Egyptian, etc., and by long experience buyers have become very expert in distinguishing samples by consideration of their physical characteristics, such as colour, weight, porosity, friability, appearance when rubbed, etc.

A precise estimation of the amount of colouring matter contained is, however, readily carried out, and such should always be made.

Examination of Indigo.—The useful constituent in commercial indigo, indigotin, varies in amount in different samples from 30 to 80%. The only other useful constituent is indirubin, which is present in amount varying from less than 1% to 10%. There is also present indigo-brown, a glutinous substance named ***indigluten***, with other organic impurities, moisture, and mineral matter.

Estimation of Moisture.—0.5 grm. of the finely powdered sample is dried to constant weight at a temperature of 105°.

Estimation of Mineral Matter.—1 grm. of the finely ground sample is carefully ignited. In the case of pure qualities the ash is frequently as low as 3%, but in inferior kinds the amount may reach as much as 25 to 30%.

Estimation of Indigotin.—A large number of different methods have been proposed for estimating the percentage of indigotin in commercial indigo. They may be conveniently classified as follows:

(a) Colorimetric tests.
(b) Comparative dyeing trials.
(c) Extraction by solvents.
(d) Sublimation.
(e) Oxidation tests.
(f) Reduction tests.

Of these, the two latter only need be considered in any detail, but short reference will be made to the others.

(a) Colorimetric Tests.

Equal weights of pure indigotin and of the sample under examination are dissolved in sulphuric acid. The sulphindigotic acid is purified (see oxidation tests) and the relative intensity of colour of the solutions determined in a Dubosc colorimeter or Lovibond's tintometer. This method of estimation is liable to inaccuracies due to coloured impurities in the natural indigo, which are difficult to remove. It is also affected by any difference in amount of indigo red in the standard and in the sample. C. H. Wolff (*J. Soc. Chem. Ind.*, 1884, **3**, 156) states that this difficulty can be avoided by observing the absorption-spectrum (1 in 800,000).

(b) Comparative Dyeing Trials.

The samples of indigo are dissolved in sulphuric acid and made into standard solutions (see oxidation tests, page 396) containing 1 grm. of the sample per litre. 10 grm. of wool are then dyed with 500 c.c. water containing 50 c.c. of the solution with the addition of 2 c.c. of 10% sulphuric acid. The dyed patterns are compared with standard patterns dyed in a similar manner with solutions of pure indigotin.

Grossmann (*J. Soc. Dyers and Colourists*, 1897, **13**, 124) proposes a special form of apparatus for carrying out these tests.

Dyeing trials are subject to the same inaccuracies as colorimetric tests.

(c) Extraction by Solvents.

A large number of processes for estimating indigotin have been based on the extraction of the indigotin by volatile solvents.

Extraction by Aniline.—Hoenig's process (*Zeitschr. angw. Chem.*, 1889, 10) is as follows: 0.8 mg. of indigo is mixed with 2.5 grm. finely powdered dry pumice stone. The mixture is extracted with 50 c.c of aniline oil in a Zulkovsky-Wolfbauer apparatus for 1 hour. The mass is then removed, washed with alcohol, dried, powdered, returned to the apparatus, and extracted a second time. The mixed extracts are evaporated in an oil bath to about 10 c.c. then mixed with 50 c.c. of absolute alcohol. The precipitated indigotin is collected on a weighed filter, washed with alcohol, dried at 110°, and weighed. The method is not very accurate.

Brandt (*Rev. Gén. Mat. Col.*, 1897, **1**, 43) similarly extracts with aniline oil in a Soxhlet apparatus. After extraction the aniline is removed by treatment with dilute hydrochloric acid and the indigo collected on a tared filter, washed with boiling water, then with cold alcohol, dried, and weighed.

Extraction by Phenol.—Brandt (*Rev. Gén. Mat. Col.*, 1898, **2**, 26) later states that extraction with aniline destroys a portion of the indigotin, and proposes to use 30 grm. of phenol for 0.2 grm. indigo. The extraction is complete in half an hour. After cooling, a solution of 20 grm. of sodium hydroxide in 250 c.c. water is added, the indigo is collected on a tared filter, washed with boiling water until neutral, then with alcohol, and dried.

Extraction by Naphthalene.—Schneider (*Zeitschr. anal. Chem.*, 1895, **34**, 347) extracts 1 grm. indigo with 50 grm. naphthalene, until the drops which fall from the extractor are colourless. After cooling, the indigotin is precipitated by adding ether, then collected, washed with ether, dried, and weighed. The extraction occupies 5–6 hours, and a certain amount of destruction of indigotin occurs, for which a correction ammounting to 0.1–0.4% is made. The whole of the materials and apparatus must be carefully dried to avoid the danger of explosion.

Extraction by Nitrobenzene.—Gerland (*J. Soc. Chem. Ind.*, 1896, **15**, 17; 1897, **16**, 108) has devised a simple apparatus for extracting indigo with nitrobenzene. 0.5 grm. indigo is placed in a filtering tube and extracted with 25 c.c. nitrobenzene for 1 hour. The indigotin separates in beautiful crystals, only a small proportion remaining in solution; to save the trouble of recovering this, nitrobenzene saturated with indigotin in the cold is used for the extraction. The indigotin is collected on a tared filter, washed with benzene, and dried. Although apparently pure, the crystals contain 3–6% impurity, and a prolonged treatment with hydrochloric acid containing a little hydrogen peroxide is necessary before weighing.

Extraction by Acetic Acid.—Brylinski (*Rev. Gén. Mat. Col.*, 1898, **2**, 52) extracts 0.2 grm. of indigo with 50 c.c. glacial acetic acid in a Soxhlet flask, using a thimble filter. The acetic acid is boiled by a free flame, and the extraction continued until the solvent passes through colourless. After cooling the acetic acid is diluted with four times its volume of water, which precipitates the indigotin in flakes. The liquid is passed through a tared filter and the indigotin washed first with boiling water, then with alcohol, finally with ether, dried and weighed.

(d) Sublimation of the Indigotin.

No satisfactory quantitative results can be obtained by this process.

(e) Oxidation Process.

In these processes the indigotin is first converted into a sulphonic acid, which is purified if necessary, made into a standard solution, and and a portion then titrated with a standard solution of some suitable oxidising agent such as potassium permanganate; the oxidising agent being itself standardised by means of a solution of pure indigotin.

The process involves four stages; (1) preparation of the sample; (2)

dissolving the indigo in sulphuric acid; (3) purification of the sulphonic acid; (4) titration with a standard oxidising agent. This method of estimating indigotin has been mainly developed by Rawson, who originally proposed the permanganate method (*J. Soc. Dyers and Col.*, 1885, **1**, 74).

(1) **Preparation of the Sample.**—Since various chests of the same manufacture or even various lumps in the same chest of indigo may differ in percentage of colouring matter, as great a variety of samples as possible should be obtained from the bulk. These should be coarsely ground, well mixed, and a small portion finely ground to an inpalpable powder. Moisture should then be estimated by drying at 105, and the dried sample used for Process 2.

(2) **Dissolving the Indigo in Sulphuric Acid.**—Rawson mixes 0.5 grm. of the finely powdered indigo with its own weight of ground glass in a small mortar. The mixture is gradually added to 20 c.c. of concentrated sulphuric acid contained in a cylindrical porcelain crucible (capacity 30 c.c.) constantly stirring with a glass rod. The mortar is rinsed with a little powdered glass which is added to the mixture and the crucible is heated for 1 hour in a water oven at 70°. Under these conditions indigotindisulphonic acid is exclusively formed. The mass is diluted with water, made up to 500 c.c. and filtered to remove the glass and certain insoluble impurities.

Instead of the crucible, Schulten prefers the use of small glass-stoppered bottles which can be readily shaken, and recommends that the suphonation be carried out for 15 minutes at the temperature of the boiling water bath.

Bloxam (*J. Soc. Chem. Ind.*, 1906, **25**, 735) recommends that the indigotin be converted into the tetrasulphonic acid, which eliminates the necessity for subsequently purifying the sulphonic acid by salting out as described in Process 3. 1 grm. of indigo is mixed with 2–3 grm. of sand, and placed in a 1-oz. spouted beaker. 5 c.c. of fuming sulphuric acid (25% SO_3) are added and the mixture stirred with a glass rod. The beaker is heated in the water oven for half an hour, then cooled, and the contents diluted to 500 c.c. 100 c.c. of this solution are mixed with 80 c.c. of a solution containing 450 grm. potassium acetate per litre. The mixture is warmed until the precipitate which is first formed redissolves. The solution is then cooled and left for 1 hour in a vessel containing ice and water. The potassium tetra-sulphonate which crystallises out is collected in a Gooch crucible and

washed with an ice cold solution containing 225 grm. potassium acetate and 12 c.c. glacial acetic acid per litre. The precipitate is finally dissolved in hot water and the solution made up to 500 c.c.

(3) **Purification of the Disulphonic Acid.**—Several of the impurities contained in natural indigo are rendered soluble by the sulphuric acid treatment, and thus appear in the final solution. They further react with potassium permanganate or other oxidising agent, and thus introduce errors into the estimation. Various methods of purifying the indigotin disulphonic acid have therefore been suggested.

Salting-out Method.—50 c.c. of the filtered solution of indigo are mixed with 50 c.c. of water and 32 grm. of salt. The liquor which is thus almost saturated with salt is allowed to stand for 1 hour. The precipitated indigotin sodium disulphonate is collected and washed with about 50 c.c. of saturated salt solution. It is then dissolved in salt water, cooled, mixed with 1 c.c. sulphuric acid, diluted to 300 c.c. and titrated as described under 4. A correction amounting to 0.001 grm. is required in order to allow for the small quantity of sodium indigotindisulphonate which dissolves in a saturated solution of common salt.

Barium Chloride Process (Rawson, *J. Soc. Chem. Ind.*, 1899, **18**, 251).—After dissolving the indigo in sulphuric acid and diluting with water, but before making up to 500 c.c., 10 c.c. of a 20% solution of barium chloride are added. The solution is then diluted to 500 c.c. and well mixed. On standing, the barium sulphate formed subsides and carries down with it the suspended impurities. In 15 to 20 minutes the clear solution may be withdrawn from the top of the flask for titration.

Calcium Carbonate Process (Grossmann, *J. Soc. Chem. Ind.*, 1905, **24**, 308).—About 6 grm. of pure calcium carbonate is employed instead of the barium chloride in the last described process.

Bergtheil and Briggs (*J. Soc. Chem. Ind.*, 1906, **25**, 729) state that both barium chloride and calcium carbonate cause a precipitation of colouring matter, and suggest the use of freshly precipitated barium sulphate. According to these authors precipitation either with salt or barium chloride gives satisfactory results.

Donath and Strasser (*J. Soc. Chem. Ind.*, 1894, **13**, 426) propose to remove the impurities by extracting the ground indigo in a Soxhlet apparatus with dilute hydrochloric acid, hot water, and finally with alcohol and ether, before solution in sulphuric acid.

(4) **Titration with Standard Oxidising Solution.**—Many oxidising agents have been suggested for titrating indigo, but potassium permanganate solution is now universally preferred.

Rawson recommends the following procedure: 50 c.c. of the sulphindigotic solution after purification by one or other of the processes described under (3) are diluted to 300 c.c. with distilled water and placed in a white porcelain dish. A solution of N/50 potassium permanganate (0.632 grm. per litre) is gradually run in from a burette until the liquor which at first becomes green, changes to a light yellow colour. With pure indigotin the end-point is quite sharp, but with low qualities of indigo some practice is necessary in order to obtain concordant results. The end-point is also more difficult to determine in the case of indigos containing notable quantities (more than 1%) of indigo red. In such cases the indirubin must be separately estimated by the process described below.

The indigotin factor of the permanganate solution is obtained by dissolving 0.5 grm. of pure indigotin prepared as described on page 384 in sulphuric acid, diluting and titrating as above described.

It is very necessary that the prescribed conditions should be closely adhered to throughout.

The oxidation of the indigo by the permanganate is represented by the equation $5C_{16}H_8N_2O_2(SO_3H)_2 + 4KMnO_4 + 6H_2SO_4 = 5C_{16}H_8N_2O_4(SO_3H)_2 + 2K_2SO_4 + 4MnSO_4 + 6H_2O$.

According to this equation 4 molecules (316 parts) of potassium permanganate are equivalent to 5 molecules (565 parts) of indigotin, but experiment shows that at the dilution necessary to obtain a satisfactory end-point the permanganate factor is somewhat lower than theory requires. Hence the necessity for obtaining the indigo factor of the permanganate by standardising with pure indigotin under the prescribed conditions.

Analysis of Indigo Rich in Indirubin.—A considerable amount of the natural indigo now on the market contains 5 or even 10% of indirubin, and the analysis of such samples by the ordinary permanganate process is not easy.

As already stated, indirubin is more resistant to the action of oxidising agents than indigotin. Both substances are sulphonated and appear together in the solution to be titrated. As the permanganate is added, the blue colour due to the indigotin is first destroyed and the liquid which first assumes a dirty green or brownish colour

changes to crimson when the whole of the blue is oxidised. Further additions of permanganate eventually destroy the indirubin, but there is an obvious difficulty in distinguishing between the crimson colour due to indirubin and the very similar colour due to excess of permanganate. The end-point is thus frequently a matter of much uncertainty.

In the case of fairly pure indigo practice will, however, enable an approximate determination of indigotin and indirubin by direct titration with permanganate.

Usually, however, it is more satisfactory to extract the indirubin from the sample before sulphonating.

Koppeschaar (*Zeitschr. anal. Chem.*, 1899, **38**, 1) extracts the indigo with glacial acetic acid, and estimates the indirubin colorimetrically against a standard solution of indirubin in the same solvent.

Rawson (*J. Soc. Chem. Ind.*, 1899, **18**, 252) uses ether and proceeds in a similar manner.

Gardner and Denton (*J. Soc. Dyers and Colourists*, 1901, **17**, 170) made an investigation with various solvents and pointed out that ether when pure has little solvent action on indirubin. They recommend commercial acetone as the most satisfactory solvent. 0.2 grm. of the finely powdered and dried sample is boiled for half an hour with 100 c.c. commercial acetone using a reflux condenser. After cooling, the solution is diluted to 200 c.c. with a 10% salt solution, which percipitates the small amount of ind'gotin dissolved and also some brown impurities. After shaking, the solution is allowed to stand for 5 minutes, filtered, and the indirubin estimated colorimetrically by comparison with a standard solution of pure indirubin prepared with acetone and salt solution in the same way.

Bloxam and Perkin (*Trans.*, 1910, **97**, 1460) recommend pyridine as the best extractive agent, and point out that the solvent action of acetone is due to the alcoholic impurity contained in the commercial solvent. Their process is carried out as follows: 0.25 grm. of the finely sieved and dried indigo is mixed with 25–30 grm. of purified sand in a small beaker. A thin-walled glass tube (the "container") about 25 x 90 mm. is closed at one end by a piece of cotton cloth fastened round with silk cord (wire must not be employed). A layer of asbestos is then placed in the tube and the sand and indigo mixture is poured in with the aid of a Gattermann funnel, the last traces of indigo being removed from the beaker by sand or asbestos. The upper surface of the indigo mixture is covered with a layer of sand and loose asbestos.

The container is placed in a Soxhlet tube so as to rest on 2 or 3 glass marbles to facilitate drainage. The tube is then extracted with pyridine for about half an hour or until the liquid possesses the blue colour of pure indigotin. The pyridine extract is distilled to a small bulk and finally treated with boiling water and again distilled until the last traces of pyridine have disappeared. On cooling, the indirubin and indigotin, together with some indigo brown, are precipitated and are collected in a Gooch crucible lined with asbestos. They are then treated with hot 15% hydrochloric acid to decompose any calcium salt of indigo brown present, then washed with a hot 10% sodium hydroxide solution which completely dissolves the brown impurity. The product is finally treated with 1% acetic acid, the crucible placed in a small beaker, and after drying, 5 c.c. of pure sulphuric acid are added. On heating the mixture for half an hour, both indigotin and indirubin are sulphonated. The mixed sulphonates are dissolved in hot water, filtered, and made up to 250 c.c. The quantity of each colouring matter present is then estimated colorimetrically by comparison with standard mixtures of pure indigotin and indirubin sulphonic acids. The best dilution is usually about 5 c.c. of the above solution in 200 c.c. of water, but with small amounts of indirubin a greater concentration is necessary.

Since only a portion of the indigotin is extracted from the original sample, the remainder is sulphonated and estimated either colorimetrically or by means of potassium permanganate.

Other oxidising agents, such as potassium dichromate, are less suitable for the titration of indigo as the end-point is less sharply defined.

Analysis of Indigo Containing Yellow Colouring Matter.—It has already been stated (page 389) that many samples of indigo contain a yellow colouring matter, *kæmpferol*, and this interferes with the permanganate and many other processes of estimation. Before testing it is therefore desirable to determine whether this substance is present. A small quantity of the powdered indigo is sprinkled on the surface of a few c.c. of ammonia in a porcelain dish when if indigo yellow is present a yellow solution is obtained.

When this occurs the weighed amount of the sample is treated with a warm dilute solution of ammonia (or with alcohol or ether) to remove the yellow, then collected on an asbestos filter, washed, dried, and dissolved in sulphuric acid in the usual way.

(f) Reduction Tests.

There are two methods of estimating indigotin by the use of reducing agents:

(1) The indigo is sulphonated as in the case of oxidation tests, and then titrated with a standard reducing solution.

(2) The finely ground indigo is treated direct with a suitable reducing agent in the presence of alkali, under which conditions the blue colour of the indigotin disappears and indigo white is formed.

The amount of indigotin may be estimated either by (a) noting how much of a standard solution of the reducing agent is required to completely destroy the blue colour of the indigotin or (b) by completely reducing the indigotin to indigo white then re-oxidising, collecting, and weighing the indigotin.

Reduction of Sulphonic Acids.—Müller (*Ber.*, 1880, **13**, 2283) reduces indigotindisulphonic acid by means of a standard solution of sodium hydrosulphite ($Na_2S_2O_4$). This process is suitable only when a long series of estimations have to be made, since the apparatus required is somewhat complicated. The process is, however, capable of great accuracy, and is carried out as follows:

Preparation of Sodium Hydrosulphite.—This solution may be prepared by the action of zinc powder on sodium hydrogen sulphite (v. sodium hydrosulphite) or more conveniently by dissolving about 3 grm. of solid hydrosulphite powder (B. A. S. F.) with the addition of 2 grm. sodium hydroxide, in a litre of water.

Standardising the Hydrosulphite.—This may be done either by means of pure indigotin or ammoniacal copper sulphate, using indigotin disulphonic acid as indicator in the latter case. The standard solution is prepared to contain either, 1 grm. of pure indigotin (converted into disulphonic acid) per litre or 1.904 grm. of pure crystallised copper sulphate + 100 c.c. strong ammonia per litre. These solutions are equivalent.

50 c.c. of the standard solution of indigotin are placed in a wide-mouthed 200 c.c. flask fitted with an india-rubber stopper perforated with 3 holes. Into one hole is fitted the tip of a glass-stoppered burette containing the hydrosulphite solution. The other two holes serve for the entry and exit of a current of coal gas, since it is essential that the process should be conducted in the absence of air. Air must also be excluded from the hydrosulphite burette, the upper portion

being supplied with the neutral atmosphere by suitable means. It is usually connected with a stock bottle containing a further supply of hydrosulphite.

The flask is boiled to expel air, and then allowed to cool, coal gas being admitted. The solution of hydrosulphite is now gradually run in until the indigotin is just decolourised. Under the conditions named, each c.c. of hydrosulphite used corresponds to $\frac{0.05 \text{ grm.}}{n.}$ indigotin, n indicating the number of c.c. of hydrosulphite used.

If ammoniacal copper sulphate is used for standardising the hydrosulphite, the cork should be provided with a fourth hole, in which is placed a second burette containing indigo solution to use as indicator. A few drops of this are added when the copper solution is almost decolourised, in order that a sharp end-point may be obtained. In other respect the process is carried out exactly as above described.

Titration of the Sample.—This operation is carried out in the same way as used in standardising the hydrosulphite. 0.5 grm. of the sample of indigo is dissolved in sulphuric acid and made up to 500 c.c. as in the permanganate process, 50 c.c. being then titrated with hydrosulphite until decolourised.

In a sample of indigo containing much indigo red, the indigotin becomes first decolourised and at this stage the liquid assumes a reddish-violet colour. By further titration, the indirubin is attacked and a yellow solution is obtained. In this way the amount of each of the two colouring matters can, with practice, be approximately ascertained.

In the case of pure qualities of indigo, the fully reduced liquid possesses a pale yellow colour, but with low qualities it finally assumes a brownish-yellow appearance.

Binz and Kufferath (*Färb. Zeit.*, 1903, 225) recommend that the titration with hydrosulphite be carried out *in vacuo* instead of in the presence of an inert gas.

Gerland (*J. Soc. Chem. Ind.*, 1896, **15**, 15) prefers to convert the indigotin first into monosulphonic acid, from which impurities are separated, by filtration through sand. The monosulphonic acid is then precipitated by addition of water, collected, dried, and converted into the disulphonic acid, which is then titrated with hydrosulphite solution.

Titanous Chloride Method.—Knecht (*J. Soc. Dyers and Col.*, 1904, **20**, 97; 1905, **21**, 292), who has worked out this process, states that it

has the advantage that titanous chloride is much more stable than sodium hydrosulphite. 50 c.c. commercial titanous chloride (20% solution) and 50 c.c. strong hydrochloric acid are boiled together, cooled, and made up to 2 litres. This solution is standardised by means of pure indigotin or ferric iron, 262 parts of indigotin corresponding to 112 of iron (Fe). Knecht found that the impurities present in natural indigos obscure the end-point, and recommends Grossmann's method of purification with calcium carbonate. The process is carried out as follows:

1 grm. of indigo is sulphonated with 5 c.c. of 100% sulphuric acid at 90° for 1 hour. The solution is diluted, poured into a 500 c.c. flask, 12 grms. of chalk are slowly added, and after the evolution of carbon dioxide has ceased the liquid is cooled and made up to 500 c.c. 50 c.c. of the clear solution are run into a flask, and 25 c.c. of a 20% solution of Rochelle salt added. The flask is provided with an india-rubber stopper containing 3 holes, two for entry and exit of carbon dioxide and the third for the burette containing the titanous chloride. After the air has been displaced the titration proceeds until the blue colour changes to yellow. This process gives very satisfactory results.

Gravimetric Reduction Process.—The earliest methods for the estimation of indigo were based on the formation of a small vat from which, after complete reduction, a measured quantity of the solution was withdrawn, the indigotin reprecipitated by oxidation, collected, washed, dried and weighed.

Many processes based on this general idea have been proposed. The following, due to Rawson, gives satisfactory results:

1 grm. of finely powdered indigo mixed to a paste with water is placed in a 40-oz. flask with 500 c.c. of lime water. The flask is furnished with an india-rubber stopper containing 4 holes, one connected with a coal-gas supply, one being an exit, one carrying a siphon, and the fourth a stoppered funnel. The liquid is heated to about 80° then coal gas is admitted and about 250 c.c. of a solution containing 3 grm. solid hydrosulphite is run in through the funnel. The liquid, which assumes a yellow colour, is kept hot for half an hour, and after allowing the insoluble matters to deposit, 500 c. c. of hydrochloric acid off into a flask, and air is drawn through for about 20 minutes to re-oxidise the indigo white to indigotin. About 10 c.c. of hydrochloric acid is then added and the liquid heated nearly to boiling. The precipitate is collected on a tared filter, washed with hot dilute

hydrochloric acid, then with water, dried, and weighed. The remaining solution in the original flask is measured and the amount of indigotin in the total calculated. Greater accuracy is obtained by dissolving the recovered indigotin in sulphuric acid and titrating with permanganate.

H. M. Rau (*J. Amer. Chem. Soc.*, 1885, **7**, 16) uses grape-sugar and sodium hydroxide in forming his vat, and otherwise proceeds as above.

F. A. Owen (*J. Amer. Chem. Soc.*, 1888, **10**, 24) recommends a vat containing zinc dust and ammonia.

G. Engel proposes the use of vanadyl sulphate. 10 grm. of ammonium vanadate are dissolved in 100 grm. of concentrated sulphuric acid with the aid of heat. The red solution obtained is poured into 2 litres of water at 50°. To this are added 50 grm. zinc powder. The purplish-blue solution is filtered and cooled. The titration is carried out exactly as with hydrosulphite.

Other Methods of Analysis.

Möhlau and Zimmermann (*Zeitschr. Farb. Text. Chem.*, 1903, **3**, 189) convert indigotin into the monosulphonic acid by heating 0.1 grm. of the finely ground sample for 15 minutes with 50 c.c. of a mixture of 100 c.c. glacial acetic acid and 4 c.c. sulphuric acid. The solution is filtered hot and the residue washed with the warm acid mixture, until the filtrate is colourless. The filtered solution is then heated to 70° and poured drop by drop into 100 c.c. of boiling water. This hydrolyses the monosulphonic acid, indigotin being reproduced.

The process is not very satisfactory, since the final product is not pure.

F. Voeller (*Zeitschr. Farb. Text. Chem.*, 1891, **1**, 110.) proposed to estimate indigotin by determining the nitrogen content by Kjeldahl's method, the nitrogen found when multiplied by the factor 9.36 giving the indigotin. It is obviously necessary to completely remove all nitrogenous impurities from natural indigo before carrying out this method, and this is found to be impracticable.

Estimation of Indigo on the Fibre.—Vat-dyed indigo is found on all materials—cotton, wool, and silk—and may be estimated in several ways. Since indigo is usually associated with other colouring matter the latter should first be removed where possible by boiling the fabric successively with dilute sulphuric acid and dilute ammonia so long as

any colour is removed. The fabric is then dried and treated as follows: For wool fabrics the dry material is treated with sulphuric acid as in the formation of indigotin disulphonic acid (see page 394) the solution is filtered through glass wool and the indigotin determined either colorimetrically or by means of permanganate.

For cotton, Knecht's process (*J. Soc. Dyers and Col.*, 1909, **25**, 135 and 160) should be used. About 4 grm. of the material are treated with 25 c.c. of 80% sulphuric acid at 35 to 40°, for about 10 minutes. This dissolves both the cotton and the indigo. The solution is diluted to about 120 c.c. with water and boiled for a few minutes. This precipitates the indigotin which is filtered off through a Gooch crucible lined with asbestos or silica. The indigotin is washed, dried, sulphonated and estimated in the usual way.

Indigo may also be estimated on dyed fabrics by extracting it by means of volatile solvents (see indigo analysis, page 392), the most satisfactory solvents being nitrobenzene, phenol, or glacial acetic acid.

LOGWOOD.

Logwood is the product of a large leguminous and rapidly growing tree, *Hæmatoxylon campechianum*. It was originally imported from the Bay of Campeachy, but the supply now chiefly comes from Jamaica and Honduras. It is also exported from San Domingo, Cuba, etc.

When first cut down the wood has a yellowish-brown colour, but on exposure to the atmosphere it gradually develops superficially a rich brownish-red colour. It is imported in the form of rough logs, which, before use, are reduced to small chips or rasped to powder, these products being distinguished respectively as "chipped," and "rasped" or "ground" logwood.

Logwood extracts are obtained by treating the chipped wood with water, which extracts about 15% of the weight of the wood.

Colouring Matter of Logwood.—The freshly chipped wood contains from 5–10% of a colourless compound, *hæmatoxylin*, $C_{16}H_{14}O_6$, which when pure forms white prismatic crystals. It is slightly soluble in cold and easily in hot water, alcohol, ether, or CS_2. On fusing with alkali hydroxide it yields pyrogallic acid, $C_6H_3(OH)_3$. Hæmatoxylin has no dyeing power. It has feebly acid properties and is not a glucoside (Gardner, *Dyer and Calico Printer*, 1891, **11**, 8). In the presence of alkali, it rapidly absorbs oxygen and is converted into the

true colouring matter, *hæmatein*. This change is brought about more or less completely during the so-called "ageing" of logwood, a process which consists in subjecting the moistened ground wood to atmospheric oxidation by exposing it in heaps in a warm room. Hæmatoxylin is thus the *colouring principle* of logwod from which the true *colouring matter*, hæmatein, is formed by oxidation. *Hæmatein*, $C_{16}H_{12}O_6$, when pure, forms brownish-red crystals. It is almost insoluble in cold water, but is soluble in hot water or alcohol. It behaves as a weak acid and forms soluble salts with sodium, potassium, and ammonium, which possess a beautiful purple colour. In conjunction with the heavy metals it forms strongly coloured insoluble salts, or colour-lakes, upon the formation of which the value of logwood as a dyestuff depends. The iron-lake is black; the chromium-lake, blue-black; the copper-lake, greenish-black, and the aluminium-lake, purplish-blue. Hæmateinis somewhat easily attacked by oxidising agents with formation of brown worthless products. It is decomposed by hot sulphuric acid, but is soluble unchanged in cold conc. sulphuric acid with a brownish-red colour. In "overaged" or "burnt" logwood the hæmatein has been more or less destroyed by oxidation. A similar defect is brought about by "overchromed" wool, in which case the excess of potassium dichromate oxidises and destroys the colouring matter.

The colour-producing substance of logwood may thus exist in 3 forms, viz., as hæmatoxylin, the colouring principle, as hæmatein, the colouring matter, and as the worthless brown overoxidation product.

Logwood Extracts.—These are now used more largely than the rasped or ground wood. They are prepared from the unaged wood by extraction with pure superheated water, the extract being concentrated in vacuum pans. The extracts are sold usually as pasty liquids of 51° Tw. ("logwood extract") or in the solid form ("solid logwood extract"). The extract, as first formed, contains essentially hæmatoxylin, but many forms of oxidised extract in which the colouring matter is chiefly present in the form of hæmatein are now on the market. These are sold under such names as "hæmatein crystals," "oxidised logwood extract," "logwood extract for wool," etc.

The unoxidised extracts are generally used in cotton dyeing, the oxidised extracts are employed for wool and silk.

In its commercial form logwood extract may be stored for some time without deterioration, but when diluted it somewhat rapidly fer-

ments with destruction of the colouring matter. Logwood is chiefly employed for dyeing blacks, or as the darkening constituent in browns, olives, greys, etc. On cotton and silk it is used in conjunction with iron mordants, on wool usually with potassium dichromate as mordant, though iron blacks on wool are not infrequent.

Certain "direct blacks" for wool were much employed a few years ago. These were sold in the form of pastes or dry powders containing logwood extracts, ferrous sulphate, and oxalic acid, the latter acting as a solvent for the insoluble hæmatein-iron lake.

Valuation of Logwood and Logwood Extract.—Since logwood and logwood extract contain a large amount of coloured soluble substances other than colouring matter, it is obviously impossible to estimate the amount of the latter by any direct colorimetric process. Further, hæmatoxylin is a colourless substance, though it is readily converted into hæmatein, and this change frequently takes place during the actual dyeing process. Any exact estimation of the value of a sample of logwood should thus involve a determination of (a) hæmatoxylin, (b) hæmatein, and (c) impurities; but no satisfactory method of doing this has been devised.

The most reliable means of estimating the value of samples of logwood or logwood extract is by means of comparative dye trials carried out under the exact conditions under which the dye is to be practically employed. It is essential that strict attention be paid to this point since the practical value of any sample depends largely on the process used in applying it.

For instance, in the case of two samples containing the same amount of colouring matter, but in the one case chiefly in the form of hæmatoxylin and in the other of hæmatein, the former would be most valuable in cotton dyeing, whereas the latter would be the best for use in wool dyeing; though by slight modifications of process either could be used for either purpose. The nature of the impurities may also have an important influence upon the value for a particular purpose. For example, a logwood extract to which 20% of chestnut extract had been added would be unsuitable for use in wool dyeing, since boiling with tannin matters tends to give wool a harsh feel. For use in the black dyeing of cotton this extract might, however, be quite satisfactory.

In carrying out dyeing experiments, amounts should be used which will produce greys only, in order that small differences may be obvious.

In testing samples for use in wool dyeing, the yarn or cloth in 10 grm.

lots is mordanted with 3% of potassium dichromate, raising to the boil in about half an hour and boiling for half an hour. The necessary number of hanks may conveniently be mordanted all in the same vessel in order to ensure equal treatment. Then, after washing, the mordanted patterns are separately dyed with about 10% of ground logwood or 2–3% of logwood extract. Similar experiments may be carried out on wool mordanted with 3% potassium dichromate and 1% sulphuric acid (oxidising mordant) and 3% potassium dichromate with 4% tartaric acid (reduced mordant). By comparing the 3 sets of dyed patterns some idea of the degree of oxidation as well as of the amount of colouring matter present will be arrived at.

Hæmatoxylin will produce a very pale colour on the reduced mordant, but will dye up fully on the oxidising mordant. Hæmatein will dye well on the reduced mordant, but will produce a dull colour on the oxidising mordant since some overoxidation will take place.

During the "ageing" process, or in the manufacture of the extract, logwood is sometimes treated with an alkali, such as lime water, with a view of giving it a fictitious appearance of strength. If so treated, the wood yields its colouring matter more readily to water, but overoxidation and deterioration occur more readily.

Logwood extracts are frequently adulterated with molasses, dextrin, or tannin extract. For the detection of these substances 2 grm. of the extract are dried at 100° and then extracted with absolute alcohol until the latter gives no further reaction for hæmatein with sodium aluminate. On extracting the residue with water, molasses and dextrin may be detected in the usual manner. Logwood extract may normally contain 0.5 % of dextrose.

Tannin matter is also a normal constituent, but if added as an adulterant will be present in excessive amount and may be detected by the strong grey or black colour produced by a cold dilute solution of the extract upon cotton mordanted with ferric iron.

The amount of moisture in logwood and logwood extracts varies within wide limits, and should always be estimated. The presence of any considerable amount of inorganic matter such as salt, sodium sulphate, or chalk, points to adulteration.

The reactions of an aqueous decoction of logwood are due to the simultaneous presence of hæmatoxylin and hæmatein. Dilute acids turn the solution yellow, but with excess of a strong acid a red colour is produced. Hydrogen sulphide or sulphurous acid partially decol-

ourises a solution of logwood, turning it yellow. Alkalies and ammonia produce first a red, then a violet, and ultimately a brown colour; while lime, baryta, and most of the hydroxides of the heavy metals produce blue precipitates. Stannous hydroxide behaves as a base and yields a violet lake, while stannic hydroxide reacts as an acid and turns a logwood solution red. Salts of iron yield a bluish-black colouration, a reaction which is employed for producing *ink*. Mercuric chloride yields an orange, tartar-emetic a carmine, and bismuth nitrate a fine violet precipitate with logwood solution. Alum gives at first a yellow colouration, which turns red after a time; while sodium aluminate yields an abundant bluish-violet precipitate, insoluble in excess of alkali. This test is so delicate and characteristic that by means of it logwood may frequently be detected in a mixed decoction with great facility. Another characteristic reaction of logwood is the black colouration it produces with a dilute solution of dichromate. This develops slowly, and, on boiling, a black precipitate is produced.

Detection of Logwood on the Fibre.—In the absence of other colouring matters the detection of logwood on the fibre is not difficult. In the case of wool the ash obtained on ignition will probably contain chromium which may be detected by fusing the ash with potassium chlorate. If a bright yellow mass is obtained, it is dissolved in water and a few drops of acetic acid are added; a drop of lead acetate solution will then produce a bright yellow precipitate if chromium is present.

Logwood on cotton will yield on ignition an ash containing iron; the ash has a reddish-brown colour and its solution in hydrochloric acid gives a blue precipitate with potassium ferrocyanide.

The presence of chromium or iron is of course merely an indication, not a proof of the presence of logwood.

If employed in conjunction with other colouring matters, such, *e. g.*, as gallocyanin, the detection of logwood is not easy, but the following reactions of logwood will usually enable a judgment to be formed. On boiling with dilute (5%) hydrochloric acid a cherry-red solution is obtained, the fibre becoming purple or drab. On adding excess of alkali to the acid solution a deep violet colour is produced, the liquid gradually depositing a brown precipitate.

Concentrated hydrochloric acid produces a red spot on logwood-dyed material; if this spot is pressed against a piece of filter-paper it produces a red stain which turns blue if touched with a glass rod moistened with aluminate of soda.

All logwood dyes are readily bleached by hypochlorites.

The following procedure is recommended for distinguishing logwood in the presence of *Alizarin Blue*, *gallocyanin*, or *indigo*.[1]

The sample is treated in a porcelain dish with cold concentrated sulphuric acid. Indigo gives a blue solution which remains blue on dilution; Alizarin Blue, a violet-blue liquid which becomes violet-red on dilution; Gallocyanin gives a violet liquid which becomes redder on dilution; logwood gives a brownish-red solution which becomes yellow on dilution, and this yellow even in small amounts so greatly modifies the pinks due to Alizarin Blue and Gallocyanin that its detection is quite easy if comparison is made with similar solutions prepared from known dyestuffs.

With a mixture of indigo and logwood the sulphuric acid solution is green and remains green on dilution, but on passing several times through a filter the indigo is removed and the soluiton becomes yellow.

NATURAL YELLOW COLOURING MATTERS.

The following table includes the chief natural yellow colouring matters:

Commercial name	Source		Coloring principle	
	Botanical	Geographical	Name	Formula
Old Fustic; Yellow Brazil Wood.	Wood of *Morus tinctoria.*	West Indies; South America. India.	Moric acid. Morintannic acid.	$C_{15}H_{10}O_6$ $C_{13}H_{10}O_6$
Weld.	Leaves, etc., of *Reseda luteola.*	France, etc.	Luteolin.	$C_{15}H_{10}O_6$
Quercitron.	Bark of *Quercus nigra* or *Q. tinctoria.*	North and Central America.	Quercitrin. Quercetin.	$C_{21}H_{22}O_{12}$ $C_{15}H_{10}O_7$
Turmeric.	Underground stem of *Curcuma tinctoria.*	East Indies; China, Barbadoes.	Curcumin.	$C_{14}H_{14}O_4$
Gamboge.	Gum resin from *Garcinia morella.*	Siam, Cochin China, Ceylon.	Gambogin.	$C_{30}H_{35}O_6$
Saffron.	Stigmata of flower of *Crocus sativus.*	Austria, Spain, France.	Crocin. Crocetin.	$C_{44}H_{70}O_{28}$ $C_{34}H_{46}O_9$
Young Fustic; Fustet wood.	Wood of *Rhus Cotinus.*	West Indies; Levant, South Europe.	Fustin or Fisetin.	$C_{15}H_{10}O_6$
Persian Berries; Yellow Berries.	Various species of *Rhamnus.*	Spain, France, Persia, Turkey, etc.	Rhamnetin.	$C_{16}H_{12}O_7$
Annatto.	Pulpy parts of *Bixia Orellana.*	Mexico; South America.	Bixin.	$C_{28}H_{34}O_5$

[1] Manual of Dyeing, Knecht, Rawson and Loewenthal, 2d Ed., 1910, p. 348.

FUSTIC.

Fustic is also known under the names Cuba wood and yellow wood, and is the heart-wood of the tree *Morus tinctoria* or *Maclura tinctoria*. It grows in Brazil and tropical America generally, the West Indies, and India; the best qualities being exported from Cuba and Tampico. The tree attains a height of 50–70 feet, and in addition to its use as a dyestuff, is esteemed for cabinet-making purposes.

Colouring Matters.—There are two distinct colouring matters present in fustic,—*morin*, or moric acid, and *maclurin*, or morintannic acid.

Morin, $C_{15}H_{10}O_6$, is the principal colouring matter. It forms pale yellow needles, and is practically insoluble in cold water, but dissolves slightly in boiling water. It is easily soluble in alkaline solutions. When fused with potassium hydroxide it yields phloroglucinol (*sym.* $C_6H_3OH)_3$), and like most of the other natural yellow colouring matters it is a hydroxyl derivative of *flavone*, the constitution of these two compounds having been shown to be:

$$C_6H_4\left\langle\begin{array}{l} O - \underset{\|}{C} - C_6H_5 \\ CO - CH \end{array}\right. \qquad\qquad C_6H_3(OH)\left\langle\begin{array}{l} O - \underset{\|}{C} - C_6H_3(OH)_2 \\ CO - C(OH) \end{array}\right.$$

Flavone, Morin.

Morin forms compounds with metals and gives the following reactions.

Alkalies—yellow-brown solution. Alum—bright yellow precipitate. Lead acetate—orange precipitate. Copper acetate—brownish-yellow precipitate. Ferric chloride—olive-green colouration or precipitate. Stannous chloride—orange precipitate. Gelatin—no precipitate.

Maclurin, or Morintannic Acid, $C_{13}H_{10}O_6$.—This substance is much more soluble in water than morin, and is also readily soluble in alcohol and ether. The ethereal solution fluoresces green and brown. Maclurin melts at 200° and when heated with strong alkali hydroxide solution it yields phloroglucinol, $C_6H_3(OH)_3$, and protocatechuic acid, $C_6H_3(OH_2)COOH$. It dissolves in cold concentrated sulphuric acid with a yellow colour, but is reprecipitated on the addition of water. The solution in concentrated acid deposits brick-red crystals (rufimoric acid) after several days.

A solution of maclurin on reduction with zinc and sulphuric acid becomes first red and then orange in colour. The solution then

contains phloroglucinol and machromin. The latter substance becomes blue on exposure to air. Ferric chloride produces a violet colour with maclurin which changes to blue. Lead Acetate gives a yellow, and stannous chloride an orange precipitate. Gelatin produces a greenish precipitate.

The diazobenzene compound of maclurin is sold commercially under the name of *Fustine*, or Wool Yellow.

Commercial Preparations of Fustic.

Fustic, like logwood, is sold as chipped or rasped wood, and as liquid or solid extract, but is now almost exclusively employed in the extract form. Until recently fustic was subjected to the "ageing" process similarly to logwood, but no change corresponding to the conversion of hæmatoxylin into hæmatein takes place, and the only useful action appears to be the incidental one of thoroughly soaking the wood and thus rendering the colouring matter more easily extracted in the dye-bath.

Fustic extracts are manufactured in the same way as logwood extracts. The liquid extracts on standing separate into two layers, the lower layer consisting mainly of insoluble morin, and the upper liquid portion containing most of the maclurin.

Fustic extracts are frequently adulterated with dextrin, molasses, zinc sulphate, alum, tannin extracts, turmeric, or coal-tar dyes, while quercitron extract is of very common occurrence. The alum and zinc sulphate are added to enrich the colour of the extract, but they do not really increase the dyeing power.

Fustic is a mordant-dye and produces with chromium mordants an olive-brown, with aluminium and tin, yellow, and with iron and copper, olive colours. With chromium and aluminium mordants, morin is the only useful colouring matter. With iron mordant maclurin is of chief importance (Gardner, *The Dyer*, 1892, **12**, 46).

Fustic is still largely employed in wool dyeing as the yellow constituent of compound shades, but it is little used in cotton dyeing.

Examination of Fustic.—A decoction of fustic has a bitter astringent taste. Alkalies darken the solution to a reddish-brown. Dilute acids make the solution yellower and paler in colour. Sodium aluminate gives a yellow precipitate, stannous chloride or lead acetate produces an orange-yellow precipitate. Ferric chloride gives an olive-

brown colouration, which on standing deports a dark olive precipitate. The most satisfactory method of examination is that of comparative dye tests carried out on wool mordanted with potassium dichromate. Some samples give much greener shades than others, and such are most esteemed. A more accurate comparison can be arrived at by carrying out the tests on wool previously dyed a pale blue in the indigo vat, since slight differences in tint are more easily recognised in the case of the green thus produced than with the fustic yellow.

Estimation of Colouring Matter in Fustic Extract.—10 grm. of the dried sample are extracted with absolute alcohol. To the alcoholic solution hot water is gradually added until no further precipitation of morin occurs. The solution is then evaporated to about half its bulk, when most of the maclurin separates out, an addition of hydrochloric acid causing a further precipitation of maclurin.

Detection of Adulteration in Fustic Extract.—Bruhl (*J. Soc. Dyers and Col.*, 1889, 9, 124) proceeds as follows:

If present, zinc sulphate and alum may be detected in the solution obtained by extracting the dried extract with nitric acid after gentle charring.

If turmeric is present unmordanted cotton becomes yellow when boiled in a solution of the sample.

Extract of quercitron may be detected by the much deeper colour which an extract adulterated with this substance produces on wool mordanted with stannous chloride in conjunction with the paler colour which the adulterated extract produces with alum mordant. A sample of fustic extract known to be pure is necessary for comparison.

WELD.

Weld is the dried plant, *Reseda Luteola*, and, although it has now lost much of its importance, it is still cultivated in England, France, Italy, etc., to a small extent. The colouring matter, ***luteolin***, is a flavone derivative and has the composition

$$C_6H_2(OH)_2 \begin{cases} O - C - C_6H_3(OH)_2 \\ \phantom{O - {}} \| \\ CO - C - H \end{cases}$$

Is thus allied to morin (old fustic), and quercetin (quercitron bark). It forms pale yellow needles and has been prepared synthetically.

Weld produces an extremely bright yellow with alum mordant, and

is still used in conjunction with indigo vat blue for producing certain shades of green. It appears in the market as bundles consisting of the whole of the plant, and before use is generally chopped into small pieces.

Quercitron Bark and Flavin.

Quercitron bark is the inner bark of a species of oak, *Quercus nigra* or *Quercus tinctoria*, indigenous to the United States. The bark is used in the form of powder or as an extract.

Flavin is obtained by extracting quercitron bark with water at a high temperature, the solution depositing the colouring matter on cooling.

Quercitron, $C_{21}H_{22}O_{12}$, is the glucoside existing in the bark. Flavin consists essentially of this substance. It forms pale yellow crystals, and on boiling with dilute acid, splits up into the colouring matter, quercetin, and dextrose.

Quercetin, $C_{15}H_{10}O_7$, is one of the commonest yellow colouring matters in vegetable products. It is a simple derivative of flavone having the composition

$$C_6H_2(OH)_2 \left\langle \begin{array}{l} O - C - C_6H_3(OH)_2 \\ \qquad \| \\ CO - C - OH \end{array} \right.$$

and is closely allied to morin and luteolin. The use of quercitron bark and flavin has now almost entirely ceased, but when still employed it is generally in the form of extract.

These dyes are best valued by making comparative dye trials in the usual manner.

Catechu, Cutch, and Gambier.

These are obtained from various species of mimosa, acacia, and areca, growing chiefly in India. They contain large amounts of tannin matter, and varying amounts of catechu-tannic acid (see tannin matters), along with a white crystalline substance, *catechin*. There is also present a brown amorphous oxidation product. These products are used as tannin matters and also for the production of brown shades on cotton.

Catechu-tannic acid constitutes the soluble portion of the product,

and has the usual properties of a tannin, giving white precipitates with gelatin and with tartar emetic, and a green precipitate with ferric chloride. On exposure to air, particularly in the presence of alkali, it becomes oxidised to a reddish-brown substance. For the properties of *catechin* see page 28.

The dyeing value of catechu and allied products depends upon the production of the brown oxidation products of catechin and catechu-tannic acid. The only satisfactory method of valuing catechu, cutch, and gambier for use in dyeing is by means of comparative dyeing trials. These should be carried out as follows: 10 grm. cotton yarn is dyed for 1 hour at the boil with 10% of the sample. The material is allowed to cool in the liquid, then taken out, squeezed, and worked in fresh baths for half an hour with 2% potassium dichromate at 80°. A second and third hank should be dyed in a similar way in the same solutions and subsequently chromed, and a parallel series of experiments should be made with the addition of 1% of copper sulphate to the dye-bath. A comparison of the strength and exhausting powers of the samples is thus obtained.

TURMERIC.

Turmeric or Indian saffron is the tuber or underground stem of *Curcuma tinctoria* or *longa* and *C. rotunda*. The colour of the roots externally is generally greyish, but in the interior they are usually a deep yellow.[1]

According to John, turmeric root contains: yellowish volatile oil, 1%; yellowish-brown resin, 10 to 11; brown extractive matter, with dyeing properties, 1 to 12; gummy matter, 14; matter soluble in alkalies, including earthy salts, 57; and moisture, loss, etc., 7 to 5%. The presence of starch is not indicated in this analysis, though turmeric root contains a sufficient proportion for iodine solution to change the whole colour from yellow to blue.

The powder of turmeric has a strong odour and a very bright orange colour. The taste is bitter and aromatic. Cold water dissolves but little colouring matter, but boiling water extracts a larger quantity.

[1] The principal commercial varieties of turmeric are: *Chinese*, consisting of many central rhizomes with well-developed branches; *Bengal*, mostly in slender branches of a deep reddish tint; *Java*, which consists of rather small tubers and branches that are often transversely and longitudinally cut; and *Cochin turmeric*, in sections or slices of a larger tuber, some being marked with rather large depressed stem-scars.

Alcohol dissolves the colouring matter freely, and likewise takes up the greater part of the resin.

Curcumin, $C_{14}H_{14}O_4$,[1] is prepared according to Jackson and Mencke (*J. Amer. Chem. Soc.*, 1882, 4, 77) by treating ground turmeric with petroleum spirit to remove the volatile oil, and then with ether, which dissolves the curcumin together with a large quantity of resin. The product is purified by crystallisation from alcohol. Thus prepared, curcumin crystallises from hot alcohol in thick needles or prisms, which have an orange-red colour and a beautiful blue reflection. Curcumin is odourless when pure, melts at 178°, and is only slightly soluble in water, even when boiling. It is difficultly soluble in cold but more readily in boiling alcohol. The ethereal solution exhibits a strong green fluorescence. It is also soluble in wood spirit and glacial acetic acid, but only slightly so in benzene or carbon disulphide, and is all but insoluble in petroleum spirit. Strong sulphuric acid dissolves curcumin with a fine reddish-purple colour, gradually changing to black from charring, and the same effect is produced, though more slowly, by strong hydrochloric acid.

Curcumin dissolves readily with a reddish-brown colour in solutions of alkali hydroxides and carbonates, and to a slight extent when boiled with water and calcium carbonate. The ammoniacal solution redeposits curcumin on boiling. On adding a large excess of strong alcoholic potassium hydroxide to a hot alcoholic solution of curcumin, the potassium salt, $C_{14}H_{12}O_4K_2$, separates in globular radiated groups of flame-coloured crystals, which assume a claret colour when dried. The precipitation may be made more perfect by adding ether, in which the new compound is nearly insoluble, though it is soluble in alcohol and freely so in water. On exposure to air, the alcoholic solution of potassium curcumate assumes a magenta colour, probably from oxidation. When excess of potassium carbonate is added to a hot solution of curcumin in absolute alcohol, the acid salt, $C_{14}H_{13}O_4K$, is formed, and on adding ether this separates in crimson-black flocks resembling magenta.

In consequence of the sensitiveness of curcumin to alkalies, turmeric is sometimes used as an indicator of alkalinity. The yellow colour is

[1] The following structural formula has been assigned to this substance:

$$C_6H_3\begin{cases}(1)CH<\begin{matrix}C_6H_5\\COOH\end{matrix}\\(3)O.CH_3\\(4)OH.\end{cases}$$

Ciamician and Silber (*Ber.*, 1897, 30, 192) adopt the formula $C_{19}H_{14}O_4(OCH_3)_2$ for curcumin.

restored by very weak acids, and hence turmeric has been proposed for titrating fatty acids, for which purpose, however, phenolphthaleïn is better adapted (see vol. 2, and R. T. Thomson, (*J. Soc. Chem. Ind.*, 1887, **6**, 195).[1] The alcoholic solution of turmeric exhibits a well-marked fluorescence.

The most characteristic reaction of curcumin and turmeric is that with boric acid. If an alcoholic solution of turmeric or curcumin be mixed with boric acid, it assumes a deep red colour, distinct from that produced by alkalies. A convenient way of applying the test is to place a small disc of filter-paper, about 1 inch in diameter, in the turmeric tincture, and evaporate the latter to dryness at 100°. On the paper is then poured an aqueous solution of boric acid, or a solution of borax to which sufficient hydrochloric acid has been added to render it distinctly acid to litmus. The red colour is at once developed, or becomes apparent on evaporating the liquid to dryness. On now adding a drop of alkali hydroxide, a very beautiful series of colour of changes will be produced, green and purple being the most prominent. On adding hydrochloric acid a red colour is produced which is again turned green and blue on addition of excess of alkali.

The behaviour of curcumin with boric acid appears to be due to the formation of a substance called by Schlumberger *rosocyanin*, which may be prepared by treating an alcoholic solution of curcumin with boric and sulphuric acids. The liquid acquires a deep red colour, which changes gradually in the cold, and rapidly on heating, to dark red, orange, and finally to yellow. Hence the operation should be arrested when a sample is found to become blue on adding ammonia. The impure rosocyanin crystallises out as the solution cools. When pure, it forms dark red needles with a green reflection, and is insoluble in water, ether, or benzene. The alcoholic solution has an intense rose-red colour, but rapidly changes. It is turned blue by ammonia, the original colour returning on adding an acid. The alkaline solution becomes grey on exposure to air, and gives blue precipitates with lime or baryta water.

Turmeric is one of the few natural colouring matters for which cotton has a strong attraction. Cotton may be dyed without a mordant by heating in a bath of turmeric at 60°. Turmeric is also employed in paper-staining and for dyeing wood and leather; also as a colouring for

[1] Turmeric is also applicable in the presence of ammonia, to which it is not sensitive.

butter, cheese, pastry, etc. It is an important ingredient of curry powder.

Powdered turmeric is sometimes adulterated with starch and mineral matters. The *ash* should not exceed 5 to 6%. Common salt is added to turmeric to give it a brighter appearance, but interferes with some of its uses. Turmeric should be quite dry. If damp it becomes yellowish-brown, and is rendered unfit for its chief applications. The characteristics of good turmeric are a rich, deep, but bright, orange colour, and a strong aromatic, rather pungent odour. Turmeric may be valued by dyeings on white woollen cloth at 60° with and without the addition of alum.

On the fibre, turmeric is turned reddish-brown by hydrochloric acid, or an acid solution of stannous chloride, without the solution becoming coloured. Sodium hydroxide and ammonia turn the fibre bright reddish-brown, the solution becoming brownish-orange. Alcohol extracts the colour, producing an orange or yellow solution with green fluorescence. Nitric acid turns the fibre pale yellow.

GAMBOGE.

Gamboge is a gum-resin produced by trees growing in various parts of the Malay peninsula. It occurs in cylindrical, hollow, or solid rolls,[1] longitudinally striated on the surface, and either distinct or more or less agglutinated or folded together in masses. Externally it is brownish-yellow, and is covered with a yellow powder. When broken it exhibits a vitreous or conchoidal fracture, the fractured surface being opaque, smooth, glistening, and of a uniform reddish-yellow colour. The powder is bright yellow, and forms a yellow emulsion with water. Although nearly without odour at the ordinary temperature, gamboge evolves a very peculiar smell when heated. The taste is at first scarcely perceptible, but after a time it produces a sharp acrid sensation in the throat. Gamboge acts as a drastic purgative.

Gambogin or Gambogic acid, the resin of gamboge, according to Buchner, has the formula $C_{30}H_{35}O_6$. It may be obtained by precipitating the filtered alcoholic solution of gamboge by water, treating the dried precipitate with ether, and evaporating the ethereal solution. The colour is hyacinth- or orange-red, and the powder bright yellow. It softens on heating and melts at 75°–80°, solidifying to a glassy

[1] The cylindrical variety of gamboge is produced by running the juice into bamboo canes. On drying, the gamboge contracts, and consequently holes are often seen through the middle of the cylinders. Inferior gamboge often occurs in irregular masses weighing several pounds.

mass on cooling. It is tasteless, and, according to Hurst, has no purgative action. Gambogin is readily soluble in alcohol, ether, and chloroform, but is only slightly soluble in petroleum spirit. It has well-marked acid properties, decomposing carbonates of the alkali-metals at a boiling heat. It dissolves in alkali hydroxides with an orange-red colour, and is precipitated in gelatinous flakes on acidifying the solution. On adding excess of common salt to the solution of gambogin in sodium hydroxide, the sodium salt is thrown down as a red precipitate.

The wax portion of gamboge insoluble in ether but soluble alcohol, is described by Hurst as a soft brownish substance, melting readily and having a slightly bitter taste and persistent bitter after-taste, with slight purgative action. It is soluble in sodium hydroxide with a brownish-yellow colour, being reprecipitated on adding an acid.

The gum of gamboge, is a transparent, brownish mass, having a sweetish taste and slightly adhesive properties. It is soluble in water forming an opalescent solution, which is rendered clear by acids, and is not precipitated by basic lead acetate, ferric chloride, mercuric chloride, borax, or alcohol. It appears to be a glucoside.

Gamboge dissolves in alcohol, in ether, and in ammonia. The ammoniacal solution produces a red precipitate with salts of barium, yellow with those of zinc, reddish-yellow with lead acetate, and brownish-yellow with silver nitrate.

The following analyses by Christison indicate the composition of commercial gamboge:

	Pipe gamboge from Siam		Cake gamboge from Siam		Ceylon gamboge			
Resin	74.2	71.6	64.3	65.0	68.8	71.5	72.9	75.5
Gum	21.8	24.0	20.7	19.7	20.7	18.8	19.4	18.4
Starchy matter	....	....	6.2	5.0	....	....	....	....
Woody fibre	....	....	4.4	6.2	6.8	5.7	4.3	0.6
Moisture	4.8	4.8	4.0	4.6	4.6	....	....	4.8
	100.8	100.4	99.6	100.5	100.9	96.0	96.6	99.3

A sample of gamboge analysed by Hurst (*Pharm. J.*, 1889, [3], **19**, 761) contained: moisture, 2.50; mineral matter, 1.05; resin, soluble in ether, 66.05; wax, soluble in alcohol, 4.31; and gum, 26.03%; total, 99.94%.

Commercial gamboge is liable to adulteration with *mineral matters* and *starch*. The *ash* should not much exceed 1%. Starch may be

detected by exhausting with alcohol, boiling the residue with water. and adding iodine to the cooled liquid, when the well-known blue colouration will be produced if starch be present. It will be observed that the analyses of Christison of cake gamboge from Siam show a small proportion of starch.

Gamboge is not employed as a dye. It has a limited use in medicine as a purgative, and is employed as a yellow pigment in water-colour painting.

SAFFRON.

Saffron consists of the stigmata of the flowers of *Crocus sativus*, of which from 500,000 to 100,000 are required to produce 1 pound weight. It has an agreeable odour, and a bitter pungent taste.

[1]An essential oil is obtained by distilling saffron with water in a current of carbon dioxide, agitating the distillate with ether, and evaporating the ether in an atmosphere of carbon dioxide. It is a very mobile, nearly colourless liquid of the terpene ($C_{10}H_{16}$) class, having an intense odour of saffron, and very prone to absorb oxygen and become thick and brown.

If saffron is treated with ether, to remove the fat and essential oil, and the residue treated with cold water, the colouring principle, *crocin*, is dissolved. On shaking this solution with purified animal charcoal the colour is rapidly absorbed, and on filtering and boiling the charcoal with rectified spirit, it again passes into solution. The filtered liquid yields crocin on evaporation.

Crocin is a glucoside and has the formula $C_{44}H_{70}O_{28}$(?). It forms a yellowish-brown mass, the powder of which is yellow. It dissolves readily in water and dilute alcohol, but with difficulty in absolute alcohol or ether. Concentrated sulphuric acid dissolves it with a blue colour, changing to violet, cherry-red and finally to brown. Concentrated nitric acid also gives a blue colouration, changing to brown.

When crocin is hydrolysed it forms the colouring matter *crocetin*, $C_{34}H_{46}O_9$. The latter is best prepared by heating crocin with dilute hydrochloric acid in a current of carbon dioxide, when crocetin is precipitated as a red powder, scarcely soluble in water, but soluble in presence of an alkali with orange colour, and reprecipitated on adding an acid.

[1] Kayser (*J. Soc. Dyers and colourists*, 1885, 1, 43).

A second glucoside, *picrocrocin*, $C_{28}H_{66}O_{17}$, is said to be obtained in prismatic crystals, melting at 75°, and soluble in water and alcohol, on extracting dried saffron with ether for a prolonged period. When hydrolysed it splits up into a sugar and a terpene oil of a saffron odour already described.

Saffron is employed for colouring pastry, and has a limited use in medicine. It is liable to various substitutions and adulterations, which are classified by J. M. Maisch (*Analyst*, **10**, 200) as those derived from the same plant and those coming from other sources. The stigmata of which genuine saffron consists become thinner toward the leaves, terminate in a yellow thread, and three are generally united. Saffron *styles* are present in all saffron of Spanish origin to a greater or less extent, and crocus *stamens*, dyed so as to resemble the stigmata, are also met with. The *corolla tubes* of the crocus, dyed with Brazil-wood or santal-wood, are said to be frequently used for adulterating saffron. Various other coloured vegetable products are referred to by Maisch, including dyed *calendula* florets (marigold), and this may be detected by treating the suspected portions of the sample with petroleum ether, which is not coloured by genuine saffron, but dissolves the coal-tar colour with citron-yellow colour.

Safflower and *red poppy* have also been observed as adulterants of saffron. In the latter case the infusion is turned greyish-green by ammonia and bright red by nitric acid. Safflower is said to be so commonly substituted for saffron in some parts of America that the genuine substance is unknown (*Pharm. J.* 1876, [3], **6**, 950).

Mineral additions, such as chalk, gypsum, barium and sodium sulphate, etc., have been observed as adulterants of saffron, being made to adhere by means of honey, glucose, or glycerin. The ash of genuine saffron of good quality ranges from 4 to 7%, but in samples of Alicante saffron Hanbury (*Pharm. J.* 1870 [3], **1**, 241) found ash varying from 12 to 28%, the excess being due to mineral adulterants. Ingham has described a sample of saffron containing 45% of mineral impurity, besides a quantity of crocus stamens; Hart, a saffron yielding 20% of ash, the greater part of which consisted of barium sulphate; and Tanner, a sample containing a considerable quantity of a red ferruginous earth. Adrian has described a saffron yielding 26.4% of ash, containing borate, chloride, sulphate of sodium, and potassium carbonate, the last having probably been derived from tartrates. The presence of ammonium nitrate was also suspected.

Grispo found vegetable filaments of unknown origin in saffron, together with water, glucose, and barium sulphate. Kanoldt examined a factitious saffron that consisted entirely of an alga, probably *Fucus amylaceus*, which had been weighted with a coloured mixture of chalk and honey. For the testing of saffron see Dowzard, *Pharm.*, *J.*, 1898, **4**, 443; Viuassa, *Arch. Pharm.*, 1892, **231**, 353 and Nestler, *Zeit. Nahr. Deut.*, 1892, **6**, 489.

If genuine saffron be scattered on the surface of warm water, it immediately expands into a characteristic form, readily distinguishable from crocus stamens, or the florets of safflower, marigold, or arnica.

Saffron gives a fine yellow colour on silk, but is now rarely if ever used as a dye. It is still employed in medicine.

ANNATTO.

Annatto, occasionally called *arnotta* and *rocou*, is composed of the pulp surrounding the fruit of *Bixa orellana*, growing in the East and West Indies and South America. The two chief kinds are Spanish annatto, imported from Brazil, and the flag or French annatto which comes from Cayenne. Brazil annatto occurs in cakes or rolls, is hard and dry, brownish on the exterior but red inside, and with a rather agreeable odour. Cayenne annatto is a soft paste, of a bright yellow colour. It often has a repulsive urine-like odour, said to be due to the actual addition of urine to keep it moist and impart a rich colour.

Annatto contains 2 yellow colouring matters, *bixin* and *orellin*.

Bixin, $C_{28}H_{34}O_5$, the properties and chemical relationships of which have been very imperfectly examined, may be prepared by digesting annatto at about 80° with rectified spirit and soidum carbonate. The filtered liquid is treated with half its measure of water and a saturated solution of sodium carbonate. The precipitate, consisting of the sodium salt of bixin, is purified by resolution in weak alcohol and precipitation by sodium carbonate, and is then decomposed by hydrochloric acid. Bixin forms minute yellow leaflets which melt at 176°. It is insoluble in water and only slightly soluble in alcohol, benzene, carbon disulphide, or acetic acid, but is very readily soluble in ether. Bixin forms a sodium salt, $C_{28}H_{33}O_5Na$, $2H_2O$, which crystallises in lustrous red needles, very soluble in water, but insoluble in alcohol and ether. It also yields a compound, $C_{28}H_{33}Na_2O_5$, $2H_2O$, which forms a dull red powder. Bixin dissolves in strong sulphuric acid

with a bright blue colour, and on dilution with water a dark green precipitate is formed.

Orellin is a yellow substance soluble in water and alcohol, but insoluble in ether, and dyes cloth mordanted with alum yellow. It is probably an oxidation-product of bixin.

Annatto is only partially soluble in water, but more completely in alcohol. It dissolves readily but sometimes imperfectly in solutions of alkali hydroxides and carbonates, of borax, and of soap, forming liquids of orange or red colour, which furnish orange-red precipitates with acids. It gives orange lakes with alumina and ferrous sulphate, a yellowish-brown precipitate with salts of copper, and a lemon-yellow with tin salts. Concentrated sulphuric acid dissolves annatto with a deep blue colour, which gradually changes to green and violet. On adding water a deep green precipitate is formed.

Samples of annatto have been found adulterated with ochre, brick dust, sand, chalk, salt, starch, gum, turmeric and other colouring matters. It is chiefly used in the colouring of butter and cheese.

RED DYESTUFFS.

Cochineal and Lac Dye.—These are the only colouring matters of importance which are of animal origin. Cochineal is the female of the *coccus cacti*, an insect which feeds on various species of cactus, and is collected largely in Mexico, Guatemala, the Canary Islands, and Java.

The insects, which have no wings, are merely brushed off the plants and killed by stoving or boiling. The insect is dark reddish-brown in colour, and in appearance and size resembles the common ladybird. The natural appearance of the insect may usually be observed by allowing a few cochineal grains to soak for some time in water.

"Silver-grey" cochineal is produced by stove killing, "black" cochineal by water killing, the latter removing the grey powder to which the appearance of the former is due.

The dyestuff undergoes absolutely no preparation for the market, but before being used the insects are ground to powder.

Cochineal is relatively rich in colouring matter compared with most of the other natural dyes, containing from 10 to 20% of the pure substance. The latter exists in the dried insect (principally in the eggs), as a glucoside, *carminic acid*, from which the real colouring matter, *carmine red*, is readily produced.

Carminic acid, $C_{22}H_{22}O_{13}$ (?), is a purplish-red substance which forms crystalline salts with alkalies. It is soluble in water, alcohol, or benzene, but insoluble in ether. It is readily hydrolised by boiling with dilute acid, producing carmine red.

Carminic acid is found in several other insects and also in some plants, *e. g.* the *monada* and *dydima*.

Carmine red, $C_{11}H_{12}O_7$, is obtained by boiling the diluted aqueous solution of carminic acid with a few drops of mineral acid. It forms a dark purplish amorphous substance which produces colour lakes of very varied hues with different metals. The most characteristic lakes are those with the following metals: *Tin*, bright scarlet; *aluminium*, crimson; *chromium*, purple; *iron*, bluish-purple; *copper*, brown; *uranium*, grey.

When treated with nitric acid carmine red produces *nitro-coccusic acid*, $C_8H_5(NO_2)_3NO_3$, along with oxalic acid.

A saponifiable fat, *coccerin*, varying in amount from 1 to 4%, also exists in cochineal.

Although for many purposes cochineal has been replaced by artificial red dyes, it is still used to a very considerable extent in the production of scarlet cloth for dress uniforms for the British Army. It is also largely employed in the preparation of cochineal carmine, an artists' pigment which is very stable under the action of light.

Ammoniacal cochineal consists of *carminamide*, $C_9H_9O_4N$, an amino-compound of carmine red, and is produced by allowing ground cochineal to remain in contact with ammonia for several days. It dyes a beautiful purple colour in conjunction with tin mordant, but is now practically obsolete.

Examination of Cochineal.—Genuine samples of cochineal vary considerably in colouring power, the insects being killed immediately before egg laying. Cochineal is not now adulterated to the same extent as was the case when it was the chief scarlet dye available. A silver-grey appearance and additional weight is sometimes given to black cochineal by covering it with barium sulphate.

Another mode of sophistication is to partially extract the colouring matter by boiling the insects in water and then re-drying.

The relative values of samples of cochineal are best determined by a comparative dye trial, using wool previously mordanted with 4% stannous chloride and 4% cream of tartar; about 5% of the dyestuff being the most suitable amount. A satisfactory colorimetric method

may, however, be carried out as follows: 0.25 grm. of each sample is finely powdered and boiled with 200 c.c. of alcohol for 15 minutes, then cooled and made up to 250 c.c. with alcohol. 5 c.c. of the filtered solution along with 1 c.c. of 1% solution of alum is diluted to 100 c.c. with water and the relative intensity of colour is determined. The full colour develops in 2 to 3 minutes.

Mineral matter should be estimated, genuine samples containing less than 1%.

To detect cochineal in alimentary substances, E. Lagorce recommends that the substance should be dissolved in water or weak alcohol rendered faintly acid with acetic acid. The liquid is then agitated with amyl alcohol, separated and evaporated in presence of water. The aqueous solution obtained is treated with a few drops of a 3 per cent. solution of uranium acetate, when a beautiful bluish-green colouration or precipitate will be produced if cochineal be present. Acids destroy this colour, with production of the orange tint of the carminic acid. In the case of wine, the amyl alcohol employed should be mixed with an equal volume of benzene, or, preferably, toluene, as otherwise œnolin will also be taken up, and will mask the reaction of the cochineal. Ammoniacal cochineal, which has been occasionally employed to colour wine, produces a rose-violet or violet-blue lake with uranium oxide. Logwood gives a somewhat similar reaction, but may be distinguished from cochineal by the production of a purple tin-logwood lake; cochineal producing a bright scarlet tin-lake.

Cochineal carmine or carmine lake is a brilliant red pigment produced by precipitating a decoction of cochineal by alum or stannic chloride with addition of acid oxalate or tartrate of potassium. The employment of a decoction of cochineal itself, and not of carminic acid, is also a necessary condition, the nitrogenous matters being essential to its formation.[1] A sample examined by C. Liebermann (*J. Soc. Dyers*, 1885, 1, 269) contained, after drying, 3.7% of nitrogen, only 0.25% of which could be expelled by boiling with dilute alkali. The remainder appeared to exist as proteins, or probably in part as tyrosine.[2] The ash was white, and

[1] Several recipes, collected from standard works, have been published by M. Dechan (*Pharm. J.*, [3], 16, 611). The English process is said to consist in boiling 1 lb. of cochineal and ½ oz. of potassium carbonate with 7 gallons of water for 15 minutes. The heat having been withdrawn, 1 oz. of powdered alum is added, and the liquid stirred and allowed to settle. The clear liquid is decanted, ½ oz. of isinglass added, and heat applied till a coagulum forms, when the liquid is stirred briskly and allowed to settle.

[2] As albumin and gelatin are sometimes employed in preparing carmine, it does not follow that the whole of the nitrogen present had its origin in the cochineal.

amounted to 8.1%. 100 parts contained 43 of alumina and 45 of lime, 0.67 of tin oxide, and small proportions of magnesia, alkalies, and phosphoric acid. The composition of the original carmine was probably approximately: water, 17; mineral matter, 7; nitrogenous matters, 20; and colouring matter, 56%; with traces of wax.

Cochineal-carmine is liable to adulteration with starch, kaolin, vermilion, red-lead, chrome-red, etc. These admixtures may be detected by treating the sample with dilute ammonia, in which a pure sample should be completely and readily soluble. The solution of cochineal-carmine in ammonia yields no precipitate with ammonium oxalate, and the precipitate produced on adding an acid is a lake from which the colouring matter can only be set free by heating with moderately concentrated mineral acid. If the ammoniacal solution of carmine be heated on a water-bath, with constant stirring, until entirely destitute of ammoniacal odour, the product is a deep ruby-red liquid which gives no precipitate with mercuric chloride, and becomes purplish on addition of ammonia. Vermilionette, an eosin lake, can be recognized by treating the colouring matter with dilute sulphuric acid and agitating the liquid with ether, which on evaporation will leave the eosin in a condition ready for further examination.

Commercial cochineal-carmine contains: colouring matter 30 to 65, aluminium and lime 5 to 12, and moisture 2 to 20%.

Carmine is employed by artists, paper-stainers, and textile-printers.

Lac-dye is the product of *Coccus lacca*, which lives on the banyan and other trees, on the twigs of which the ova are deposited. From the mature and impregnated female insects a resinous substance exudes, which encloses the eggs. The twigs, with the attached resin are sold as *stick-lac*. If the resinous concretion be removed, powdered, and triturated with water, the greater part of the colouring matter dissolves, and the residue when dried is known as *seed-lac*. If this be melted and squeezed through cotton, it yields *shell-lac* or *shellac*, (see vol. 4, p. 67). The following figures by Hatchett indicate the relative composition of these three lacs:

	Stick-lac.	*Seed-lac.*	*Shell-lac.*
Resin	68.0	88.5	90.9
Colouring matter	10.0	2.5	0.5
Wax	6.0	4.5	4.0
Gluten	5.5	2.0	2.8
Foreign bodies	6.5	..	..
Loss	4.0	2.5	1.8
	100.0	100.0	100.0

Lac-dye is prepared by treating stick-lac with a weak alkaline solution and precipitating with alum, or with lime to which some alumina has been added.

The colouring matter of lac-dye has been investigated by R. E. Schmidt (*J. Soc. Dyers, and Col.* 1887, 3, 122), who terms it laccainic acid, an points out its close resemblance to carminic acid.

Laccainic acid, $C_{16}H_{12}O_8$, forms a brownish-red crystalline powder or crust, appearing under the microscope in well formed rhombic tables. It melts without decomposition at 180°. It is abundantly, though slowly, soluble in alcohol, and freely soluble in wood spirit, amyl alcohol, and glacial acetic acid. It is somewhat less soluble in water, with bluish-red colour, and is insoluble in benzene and petroleum spirit. It resembles carminic acid in being nearly insoluble in ether, but not precipitated on adding ether to its alcoholic solution. It is a well-defined dibasic acid, and in its reactions and the absorption-spectrum of its alkali-metal salts closely resembles carminic acid; but a difference exists between the absorption-spectra of the two substances when dissolved in strong sulphuric acid.

Schmidt gives the following results obtained by the analysis of 2 samples of lac-dye:

	1.	2.
Moisture (expelled at 100°)	9.0	11.26
Mineral matter	15.7	18.24
Coloring matter	10.4	13.20
Other organic matter	64.9	57.30
	100.0	100.00

A good lac-dye should be soft enough to be broken with the fingers, and should powder readily under the pestle. The fracture should be deep in colour, not shining and resinous. When breathed on, it should emit a strong and characteristic odor. Samples which are hard and have a resinous fracture are usually poor in colouring matter, and contain an excessive proportion of resin. The amount of this constituent may be judged of from the bulk of the precipitate produced on diluting the alcoholic solution of the lac with water.

A superior variety of lac-dye is obtainable by treating stick-lac with weak ammonia, and adding stannous chloride to the solution, when the colouring matter is thrown down as a fine red tin-lake. A lake is also obtained by substituting sodium hydroxide and alum for

the ammonia and tin salt in the above process. Lac-lake usually contains about 50% of colouring matter, 40 of resin, 9 of alumina, and 1% of impurities.

Lac-dye gives much the same colour as cochineal, but two or three times the quantity is requisite to produce the same effect.

ORCHIL AND CUDBEAR.

Purple dyes derived from lichens have been in use from time immemorial. A considerable number of species of lichen are used in the manufacture of orchil and cudbear, the chief being *Roccella tinctoria*, known as Valparaiso weed, and *R. fuciformis*, or Lima weed. Other species are collected in Sweden and in the Auvergne district.

The lichens do not contain any ready formed colouring matter but certain colourless compounds, from which colouring matter is produced by the action of ammonia and air. The principal colour-producing compounds existing in the lichens are *erythrin*, $C_{20}H_{22}O_{10}$, *lecanoric acid*, $C_{16}H_{14}O_7$, and *evernic acid*, $C_{17}H_{16}O_7$. These all yield the colouring principle *orcinol*, $C_7H_8O_2$, from which the colouring matter, *orcein*, $C_{14}H_{12}N_2O_3$, is directly produced.

Orcinol. Orcin. 3 : 5-dihydroxy-methylbenzene. $C_6H_3(CH_3)(OH)_2$.—This substance is homologous with resorcinol.

It forms six-sided monoclinic prisms, melting at 58° and containing $C_7H_8O_2+H_2O$. The crystals effloresce gradually over sulphuric acid, and more rapidly when heated to 100°. The anhydrous substance melts at about 107°, and distils with some decomposition at about 287° under atmospheric pressure, but may be obtained pure and colourless by distillation *in vacuo*. When pure, orcinol is colourless, but it acquires a pale reddish-brown colour on exposure to air. It has an intensely sweet, but unpleasantly astringent taste. Orcinol is extremely soluble in hot water, but much less so in cold. It is almost completely precipitated in fine needles when its concentrated solution is warmed with saturated brine. Orcinol dissolves readily in alcohol and ether, but less easily in hot benzene. The crystals deposited from the ethereal solution are anhydrous. It is neutral in reaction, but possesses marked acid properties. It readily decomposes sodium carbonate, and precipitates silica from silicates.

With oxidising agents orcinol yields oxalic acid. With concentrated sulphuric acid it gives a sulphonic acid. When treated with a solution

of bleaching powder, orcin yields an intense purple-red colouration, which rapidly changes to yellow. The most minute trace of orcinol may be detected by this test.

If an alkaline solution of orcinol be heated with a little chloroform, it becomes first purple-red and then bright red, and on dilution with water exhibits an intense greenish-yellow fluorescence, from the formation of homofluoresceïn, $C_{23}H_{18}O_5$. This reaction (Schwartz *Ber.*, 1880, **13**, 543) is so delicate that the compounds which yield orcinol on treatment with alkalies can readily be detected by this means in the lichens containing them, by simply boiling a few fragments of the plant with a 5% solution of potassium hydroxide, adding a little chloroform to the clear liquid, then warming the solution for ten minutes and diluting it with water.

An aqueous solution of orcinol is not precipitated by mercuric chloride, lead acetate, cupric sulphate, tannin, or gelatin. With basic lead acetate it yields a white precipitate, and with ferric chloride a violet-black colouration or red precipitate.

On addition of bromine-water to orcinol in aqueous solution, tribromorcinol, $C_7H_5Br_3O_2$, is formed, and the reaction has been recommended by Reymann for the quantitative estimation of orcinol and the assay of archil weeds. The process is carried out exactly as in the volumetric determination of phenol by bromination.

Orcein, $C_{14}H_{12}N_2O_3$, is the product of the action of ammonia and oxygen on orcinol. It forms a brown amorphous mass, having a beetle-green lustre. Orceïn is somewhat soluble in water with a red colour, but is reprecipitated from its solution by neutral salts of the alkali-metals. In ether it is insoluble, but dissolves readily in alcohol, yielding a scarlet solution. In fixed alkalies and ammonia orceïn dissolves with formation of splendid purplish-violet solutions.

Manufacture of Orchil.—The weeds are torn into small fragments and placed in iron boilers with a dilute solution of ammonia. The temperature is kept at 35–45° during from 5 to 7 days. The fermentation which ensues results in the production of orcinol, which is finally converted into orceïn. The process is controlled by withdrawing samples and testing from time to time. If the fermentation proceeds too far the colouring matter is destroyed.

The product still containing the weed residue is known as orchil paste. Orchil liquor is obtained by straining off the worthless solid residue.

Cudbear is produced by evaporating orchil paste to dryness and grinding.

Orchil and cudbear are still used to a very considerable extent on wool and silk, being applied either without or with a mordant, and in a neutral or acid bath.

Examination of Orchil and Cudbear.

Different samples of orchil or cudbear may vary much in strength, brilliancy, and hue, without being purposely adulterated. Comparative dyeing trials carried out on woollen yarn or cloth are the most satisfactory method of valuation. Dye tests should be made both in neutral and acid solution, using 3 to 5% of the dye. In the case of the neutral dyeings, about 3% of sulphuric acid should be added after removing the wool, and a second piece of wool dyed in the same vat, this rendering evident any adulteration with an acid coal-tar dye. The degree of exhaustion of the baths frequently varies much with different samples and should be investigated either by successive dyeings or by colorimetric examination of the waste dye liquors.

The most frequent adulteration is the coal-tar dye, magenta, which may be detected as follows (Breinl, *J. Soc. Dyers and Col.*, 1888, **4**, 46, improved by Rawson, *J. Soc. Dyers and Col.*, 1888, **4**, 68):

2 grm. of cudbear, or 4 grm. orchil liquor are dried and boiled with 50 c.c. alcohol for 15 minutes, and then diluted with 100 c.c. of water. 20 c.c. of a solution of basic lead acetate (sp. gr. 1.25) followed by 20 c.c. strong ammonia are added. After shaking, the solution is filtered, and the precipitate washed with a solution containing 1 part ammonia, 5 parts alcohol, and 10 parts water.

With pure cudbear the filtrate remains colourless on acidifying with acetic acid, whereas if magenta is present, a strong red colour is immediately developed. The amount is estimated by comparison with a standard solution of magenta.

This process is also applicable for the detection of Methyl Violet and Safranine, which may be distinguished by dyeing a small thread of wool in the solution and applying tests for those colouring matters.

Breinl, has also studied the reactions of a number of coal-tar colours similar in shade to orchil. Kertesz (*J. Soc. Dyers and Col.*, 1885, **1**, 217) tests for acid magenta as follows:

A small quantity of the sample is boiled with water and filtered. The filtrate is mixed with a little benzaldehyde, and stannous chloride

and hydrochloric acid are added. On shaking and allowing to stand, the lower layer of liquid will appear coloured if Acid Magenta is present.

Liebmann and Studer detect magenta and acid magenta as follows: 1 grm. of the dye is boiled with 100 c.c. of water and after cooling saturated with SO_2. Acetone is then added, when, if magenta or Acid Magenta is present, a violet colour gradually develops.

LITMUS.

Litmus.—This product is allied to orchil. It is prepared from various species of *Rocella*, *Variolaria*, and *Lecanoria* by allowing them to ferment in presence of ammonia, as in the manufacture of orchil, except that in the case of litmus potassium carbonate is likewise added. When the mass has become violet, stale urine, lime, and potassium hydroxide are added, and the mass is again allowed to ferment until it assumes a blue colour, when it is mixed with chalk or gypsum and a little indigo, and made up into small tablets.

On extracting litmus with cold alcohol, a red colouring matter is obtained, which is unaffected by acids, and yields litmus-blue and another substance on treatment with water. On evaporating this solution, and treating the residue with absolute alcohol and a little acetic acid, a scarlet colouring matter is removed, which is changed to purple by ammonia, while the pure litmus-blue remains behind as a brown powder, soluble in water to a reddish-brown solution, which is turned blue by the slightest trace of an alkali.

Azolitmin, $C_7H_7O_4N$, the characteristic colouring matter of litmus, may be obtained in a state of purity, according to DeLuynes, by digesting 1 part of orcinol with 1 of strong ammonia, 25 of crystallised sodium carbonate, and 5 of water, at 60°–80° for 4 or 5 days in a closed vessel. A blue liquid is thus obtained, which is diluted with water and slightly acidified with hydrochloric acid, when a precipitate is formed, which, after being washed and dried, is regarded as pure azolitmin.[1] So obtained, azolitmin is a reddish-brown powder, which is only slightly soluble in water and insoluble in alcohol and ether. Azolitmin appears to have the characters of a weak acid, the salts of which are blue, and the potassium compound of which exists in litmus.

[1] Kane prepares azolitmin by exhausting powdered litmus with water, mixing with clean fine sand and evaporating on a water-bath. Sufficient hydrochloric acid is added to give a red solution after the carbon dioxide has been driven off, and the evaporation is continued to dryness. The residue is washed with water and again evaporated on a water-bath, after which the sand is freed from its coating of pure azolitmin by treatment with weak ammonia, and the azolitmin is finally obtained from its solution by precipitation with sulphuric acid.

Litmus exhibits a very characteristic absorption-spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which absorbs the more refrangible end of the spectrum to a point midway between D and E. On adding a drop of ammonia to the ethereal solution the liquid becomes blue, and an absorption-band is formed, which commences at *d*, where it is extremely black, and gradually diminishes to E. On shaking the ethereal solution with ammoniacal water, the colouring matter passes into the aqueous liquid, and the blue solution shows a well-marked absorption-band at D. Addition of acid now changes the colour to red, and the band at D disappears, the spectrum of the acidified liquid resembling that of œnolin, the colouring matter of red wine.

Litmus is not employed in dyeing or calico-printing, but is used for colouring wine and vinegar, and in the laboratory is well known as an indicator of neutrality.

Litmus gives a deep blue colour with alkalies and a red with acids; alkaline carbonates also produce a blue colour. As litmus is sensitive to carbonic acid and hydrogen sulphide, when carbonates or sulphides are titrated in its presence, the carbonic acid and hydrogen sulphide gases which are liberated must be driven off by boiling before the end-point is taken. Litmus is a good indicator for titrating the acids present in the normal salts of such alkaloids as quinine, strychnine, morphine, narceine, and papaverine, since these are neutral to litmus. The alkaloids caffeine, narcotine, and theobromine are also neutral to litmus, but their salts act like a corresponding amount of the free acid. Aniline, toluidine and quinoline exhibit a neutral reaction toward litmus, and hence cannot be titrated by its acid.

MADDER.

Before the introduction of artificial alizarin in 1868, madder was the most important of the natural dyestuffs with the exception of indigo. It has now been almost entirely replaced by artificial alizarin, and used only to a very limited extent.

Madder is the ground root of the *Rubia tinctoria*, or other allied plants. The roots are dug up, ground, and stored for some time to develop the colouring matter.

The colour-producing substance exists in the root in the form of a glucoside, *rubian*, $C_{26}H_{28}O_{14}$. This substance is sparingly soluble in cold, and more easily in hot water, alcohol, and ether. During storage,

or in the dye-bath, it undergoes hydrolysis, this being chiefly brought about by the action of a specific enzyme *erythrozym*.

The chief colouring matter is alizarin, $C_{14}H_8O_4$, but small quantities of purpurin, $C_{14}H_8O_5$, are also formed. Both these colouring matters (as also a large series of derivatives from then) are now produced in large quantities by synthetic processes. (See Coal-tar Colours.)

Samples of madder are now so rarely met with that it is unnecessary to enter into detail with regard to their analysis. The comparative value is best determined by dye trials carried out on mordanted wool or cotton. In the case of wool, tests should be made both on potassium dichromate and on alum mordants.

REDWOODS.

The so-called red dye woods are now almost entirely obsolete. They are divisible into 2 groups—the *soluble* and *insoluble* redwoods. The former group comprises Brazil or Permanbuco wood, peach wood, Lima wood, and Sapan wood. These appear all to contain the same colouring principle, *brazilin*, $C_{16}H_{14}O_5$, which, by "ageing" (oxidation) is converted into the colouring matter *brazilein*, $C_{16}H_{12}O_5$, the change being analogous to the conversion of hæmatoxylin into hæmatein.

REDWOODS.

Commercial name.	Botanical origin.	Geographical origin.	Colouring principle.	
			Name.	Formula.
Soluble Redwoods.				
Brazil wood; Pernambuco wood.	Wood of *Cæsalpinia Brasileinsis* and *C. Crista.*	Brazil, Perambuco, Jamaica.	Brazilin.	$C_{16}H_{14}O_5$
Peach wood.	Wood of *Cæsalpinia echinata.*	Nicaragua, Sierra Nevada.	Brazilin.	$C_{16}H_{14}O_5$
Sapan wood.	Wood of *Cæsalpinia sapan.*	Siam, Japan, East Indies, etc.	Brazilin.	$C_{16}H_{14}O_5$
Insoluble Redwoods.				
Sandal, Santal, or Sanders wood.	Wood of *Pterocarpus santalinus.*	East Indies, Ceylon, Madagascar.	Santalin.	$C_{15}H_{14}O_5$(?)
Barwood.	Wood of *Baphia nitida.*	Sierra Leone.	....	....
Camwood, or Kambe wood.	Wood of species of *Pterocarpus.*	West coast of Africa.	....	....

The soluble redwoods are mordant dyes and produce purple shades with chrome mordant, and crimson with alum. These woods are still imported to a considerable extent, but are used in making pigments and not in dyeing.

The insoluble redwoods comprise camwood, barwood, and sandarswood. The only application of these woods in dyeing is that of "bottoming" indigo blues, the wool being boiled for some time with the wood before being dyed in the vat.

The colouring matters of these woods do not appear to be identical, but they have not been thoroughly investigated. That of sanderswood is *santalin*, $C_{15}H_{14}O_5$. Samples may be examined by dye trials made on wool mordanted with 2% of potassium dichromate.

ALKANET.

This consists of the cortical parts of the root of *Anchusa tinctoria*. The colouring matter alkannin is best obtained pure by extracting alkanet root with dilute potassium hydroxide solution, and agitating the solution with ether to remove a reddish-brown impurity. On saturating the alkaline liquid with carbon dioxide the alkannin is precipitated, and may be purified by solution in ether.

Alkannin, Anchusin, or *Anchusic Acid.*—This compound (probably either $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$) is a reddish-brown resinous substance of metallic lustre. It is insoluble in water, but soluble in alcohol, glacial acetic acid, ether, chloroform, carbon disulphide, turpentine, and fixed oils. The alcoholic solution is crimson, and is unchanged by exposure to light or by continued boiling. It gives a blue colouration with alkalies (restored to crimson by acids),[1] a bluish-violet precipitate with aluminium acetate, a crimson precipitate with stannous chloride, and a purple precipitate with stannic chloride. Lead acetate produces a blue, and iron salts a violet precipitate. Alkannin forms a diacetyl-derivative which crystallises from glacial acetic acid in brownish-yellow grains. It is evidently a derivative of methyl-anthracene, $C_{15}H_{12}$, as that hydrocarbon is formed when the colouring matter is distilled with zinc-dust. In its tinctorial properties and absorption-spectrum, anchusin resembles quinizarin.

The most characteristic test for alkanet and alkannin is the absorp-

[1] Paper impregnated with an alcoholic solution of alkannin forms the so-called Boettger's test paper. It is very sensitive to free alkalies and alkaline salts and particularly to ammonia, the slightest traces of which colour the paper green.

tion-spectrum. The solution in amyl alcohol gives the best results, and exhibits 3 equidistant bands in the blue-green. On adding ammonia these give place to 2 bands, one nearly coincident with and the other on the red side of the D line.

Alkanet root may be assayed by treating it with ether, which should extract not less than 5% of colouring matter. It was formerly used for dyeing various shades of violet, lilac, lavender, and yellow, but has been superseded for such purposes. It is used for staining wood crimson, and is employed in perfumery for colouring oils and pomades. An alkaline solution is sometimes used to colour syrups. Tincture of alkanet forms a very good substitute for litmus.

SAFFLOWER.

This consists of the bloom or petals of a plant resembling the thistle, indigenous to Egypt and the Levant, and cultivated in other countries. It varies much in quality, the Egyptian being the richest in colouring matter, and after that follow the Indian and Chinese. The colour of good safflower is a fiery red; a dull red colour is an indication of bad preparation.

Safflower contains 2 yellow colouring matters, one of which is soluble in cold water, and exists in considerable proportion (26 to 36%); the other is insoluble in water, but dissolves in alkaline liquids. Beside these, safflower contains a small proportion of a red colouring matter, carthamin, which is the only constituent of value. The proportion of insoluble yellow colouring matter varies inversely with that of carthamin.

Carthamin, $C_{14}H_{16}O_7$, the red colouring matter of safflower, forms only from 0.3 to 0.6% of the weight of the flowers. To prepare it, safflower is washed with cold water till no more soluble yellow colouring matter is removed, after which it is treated with water and 15% of its weight of crystallised sodium carbonate. The solution is strained from the insoluble portion, cotton yarn immersed in it, and the liquid acidified with citric acid. The cotton takes up the carthamin and an accompanying yellow colouring matter. When washed and treated with a weak solution of sodium carbonate, the carthamin dissolves, while the yellow dye remains fixed on the cotton. On acidifying the solution with tartaric acid, the carthamin is thrown down as a bright red, amorphous precipitate, which, when mixed with a little water,

forms the *safflower extract* or paste of commerce.[1] The product may be further purified by solution in alcohol and reprecipitating it by adding water.

Carthamin is insoluble in water or ether, but readily soluble in alcohol and in alkaline solutions. The cherry-red alcoholic solution dyes silk without a mordant, and when allowed to evaporate on glass leaves a varnish which appears red by transmitted light and a beautiful beetle-green by reflected light. On addition of an acid, the alcoholic solution of carthamin becomes yellow, and alkalies also turn it yellow or orange. The colouring matter is very unstable, and undergoes rapid alteration on exposure to air or when boiled with alcohol or water.

Carthamin has feeble acid characters. The ammonium salt yields, with stannic chloride, a yellowish-brown precipitate, with ferric chloride a brownish-red, and with mercuric chloride a red precipitate.

Carthamin dissolves with a red colour in strong sulphuric acid, probably forming a sulphonic acid, for the solution is not precipitated on addition of water.

Safflower is best assayed by a miniature dyeing operation, and by an application of the method already described for detecting and separating any objectionable yellow colouring matter.

The use of safflower has much decreased of late years, but it is still employed to some extent to dye silk, cotton, and linen various shades of pink and red. On fabrics dyed with annatto it produces a scarlet.

On the fibre, a rose, pink, or crimson colour due to safflower is immediately turned pale yellow by a single drop of alkali, and the colour is then destroyed by any further treatment. Weak acids do not affect the colour, but strong acids, chlorine, and sulphurous acid bleach it at once. Alcohol has no action, but ammonia changes safflower pink (on cotton) to a flesh-tint, and ammonium sulphide decolourises it.

[1] If the paste be triturated with French chalk and the mixture dried, a product is obtained which is employed as a *rouge*.

ANALYSIS OF COLOURING MATERIALS.

By W. P. DREAPER, F. I. C., and E. FEILMANN, B. Sc., Ph. D., F. I. C.

The number of artificially prepared dyestuffs occurring in commerce is very great and the difficulty of recognition is further increased by the practice of calling the same dyestuff by different names. In many cases also, different dyes give almost identical reactions with the standard reagents.

The methods of examining colouring matters with the view of their identification require considerable modification when the dye already exists on a fibre or fabric, as the mordant and general condition affects the character of the indications. Hence the recognition of the dyes on fabrics has been described in a separate section. In the case of a specific colouring matter it is desirable to ascertain the shade it communicates to cotton, wool or silk, as the shade which a dye will produce on a fibre can scarcely be determined from its appearance in the solid state, and in many cases cannot be predicted from the colour of the solution.

The identification of a coal-tar dye is facilitated by the employment of certain general reagents, which will generally define the substance as belonging to a definite class of chemical compounds. The colour or absorption-spectrum of an aqueous or alcoholic solution of the dye is also a valuable indication, and water and alcohol may be employed to effect a qualitative separation of mixed colours in some cases.

I. Physical Methods of Investigation.

Absorption-spectra of Colouring Matters.

A valuable aid to the recognition of many colouring matters consists in the observation of their *absorption-spectra*. For this purpose a

pocket spectroscope will often suffice, but it is better to employ a micro-spectroscope, furnished with a proper comparison-stage and reflecting prism, to allow of the spectrum of the colouring matter under examination being viewed in juxtaposition with the spectra of standard specimens of known origin.

In comparing the standard liquid with the sample, it is necessary to regulate the light, so that neither spectrum shall suffer from excess of illumination. This may be done effectually in the case of an object placed on the stage by the ordinary diaphragm attached to the microscope. The comparison stage should be furnished with a slit, giving a means of regulating the intensity of the light falling upon the comparison prism. In using the micro-spectroscope, it is usual to employ the colouring matters in the state of solution, and it is not desirable to use too high a dispersive power, as in that case the absorption-bands are apt to be imperfectly defined. The nature of the solvent is by no means an unimportant factor in the results obtained, H. C. Sorby having found that the position of the absorption-bands was in certain cases sensibly affected by the nature of the solvent employed. When possible, it is always advisable to use aqueous solutions. The liquid to be examined with the micro-spectroscope is most conveniently placed in a small cell made by cementing a piece of barometer-tube (half an inch to an inch in length) to a glass microscope slide by means of refined gutta-percha. The cement is not acted on by water, alcohol, or acid or alkaline solutions. The tube-cell being filled with the liquid, is covered with a thin piece of glass (microscopic cover-glass). This is not absolutely necessary unless some change is anticipated from the action of the air on the contents of the cell, but the precaution adds to the perfection of definition. In recording the results of a micro-spectroscopical examination, Sorby has suggested the use of an *interference-spectrum*, which divides the visible spectrum into 12 equal parts. With such an arrangement the sodium line D comes very accurately at 3 1/2, that is to say, in the middle of the fourth light space; the bands being shaded off gradually on each side, so that the shaded portions are about equal to the intermediate bright spaces. On this scale, the positions of the principal lines of the solar spectrum are about as follows:

A	B	C	D	E	*b*	F	G
$\frac{3}{4}$	$1\frac{1}{2}$	$2\frac{3}{8}$	$3\frac{1}{2}$	$5\frac{11}{16}$	$6\frac{3}{16}$	$7\frac{1}{2}$	$10\frac{5}{8}$

In using the micro-spectroscope it is desirable to perform the operations and to subject the colouring matter to the action of reagents as much as possible in the tube-cell used for the observation of the absorption-spectrum.[1]

In working with the micro-spectroscope it is very important to employ a strength of solution which will allow of the absorption-bands being well defined, and yet permit of as much light passing as is compatible with distinct absorption. This can only be ascertained by experiment in each case, a convenient plan being to employ a concentrated solution first of all, and then to dilute it with an appropriate solvent until the absorption-bands are satisfactory, noting the spectrum after each change in concentration. Solutions should be kept in small test-tubes, hermetically sealed and filled as completely as possible with the solutions; but even under such conditions many colouring matters, especially those derived from plants, undergo specific change. Hence it is unsatisfactory to comare a recently prepared solution of a colouring matter with one which has been kept some time, unless is has been distinctly ascertained by previous experience that it is not liable to suffer change by long keeping. In employing the method as a means of differentiating colours it is necessary to compare the results with those produced by the pure colouring matters.[2]

The Hilger type of *spectrometer* described in Vol. I. lends itself especially well to the rapid and accurate observation of absorption spectra. By means of it the wave length of the absorption bands can be rapidly measured. To obtain permanent photographic records of absorption spectra the various types of *spectrographs* are employed (see Vol. I., pp., 33–40). For details of observing absorption spectra of dyes see Formànek, *Die qualitative Spectralanalyse.*

The absorption-spectrum of a liquid containing two distinct colouring matters not having any chemical action on each other is identical with that which will be produced if the light traverses solutions of the two colouring matters in succession.[3] By employing a reagent which will

[1] The solid reagents should be employed in the form of coarse powder or small grains, which can be added to the solution in the tube of the cell by means of a stout platinum wire, hammered out into a spatular form at one end. The reagent is best mixed with the liquid by means of a small platinum wire, of which the flattened-out part is bent up at right angles so as to form a miniature hoe. By a vertical motion of this in the cell very speedy solution and admixture of the reagent are obtained.

[2] A large number of observations, together with valuable hints in manipulation, and an attempt at a systematic qualitative discrimination of animal and vegetable colouring matters by the micro-spectroscope, have been published by H. C. Sorby (*Proceedings of the Royal Society*, No. 92, 1867).

[3] The well-known production of green by the mixture of blue and yellow is due to this cause. All yellow solutions transmit (and all yellow pigments reflect) the greater part of the red, yellow, and green light of the spectrum, while absorbing the blue and violet.

destroy or modify one of the colours in a mixed solution without affecting the other, most valuable information may be obtained, and in researches on unknown colouring matters evidence is often thus afforded of the complex nature of the substance under observation.

P. Schoop (*J. Soc. Dyers*, 1886, **2**, 71) has described a means by which the absorption spectrum of a colouring matter may be applied to its quantitative determination. Girard and Pabst (*Compt. Rend.*, 1885, **101**, 156) have described several coal-tar dyes likely to be used for adulterating wines and syrups. In some cases they can be extracted and separated from the natural colouring matters by agitating the acidified liquid with amyl alcohol.

Formànek (*Zeits. Nahr- und Genussmittel*, 1899, 206), in his spectroscopic investigations on dyestuffs, has found that the bands of some dyestuffs in the same solvent are very close together; that some dyestuffs do not possess any absorption-bands at all; and, in cases where the dispersion is small, the absorption-bands of some dyestuffs are superposed. In order to obviate these difficulties he examined dyestuffs in different solutions, by which the positions of the bands were altered, or the same effect produced in the presence of acids or alkalies.

Fluorescence of Colouring Matters.

Many colouring matters, *e. g.*, some of the eosins, rhodamines, magdala-red, purpurin, turmeric, resorcin-blue, iris blue, etc., exhibit characteristic *fluorescence*. It is necessary that the liquid to be observed should be *perfectly clear*, as the presence of minute suspended particles often causes the production of a similar effect which may lead to erroneous conclusions. As a rule, the phenomenon may be observed by filling a small test-tube with the solution to be tested, holding it in a vertical position before a window, and observing the solution from above against a dark background. Another plan is to make a thick streak of the liquid on a piece of polished jet or black marble or on a glass plate smoked at the back, and to place the streaked surface in front of, and at right angles to, a well-lighted window. In this manner very faint fluorescence may be detected (see also *Introduction*, Vol. I, p. 40).

Most blue liquids (and pigments) absorb the green rays very imperfectly, and it is only such impure blues which produce greens on admixture with yellows. If the light which has traversed such a blue solution, *e. g.*, indigo-extract (or which is reflected from such a blue pigment) be transmitted through a yellow liquid (*e. g.*, picric acid, or an ammoniacal solution of potassium chromate), the green portion of the spectrum will be almost the only part which survives the double absorption, and hence the light transmitted appears green.

On the fibre the fluorescence of a dye is best shown on silk. Wool and artificial silk show it sometimes, but on cotton the fluorescence can rarely be observed, Rhodamines being a notable exception.

TINTOMETERS.

The different tintometers in use have been applied to the valuation of dye solutions.

It must be remembered that the actual shade of solutions of dyestuffs may vary in the presence of third substances (electrolytes, etc.). There are, however, cases where this method is of value and may be applied, but great care must be taken in its use.

A record of a definite shade of a solution (dye or otherwise) is of value, and may be used for standardising such solutions. With the Lovibond tintometer it is possible to register in terms of the coloured glasses used the colour composition of any dyed sample or solution. This may be used indirectly in the analysis of dye materials where their tinctorial value is desired for future comparison with other samples of dyestuffs or dyed fabrics.

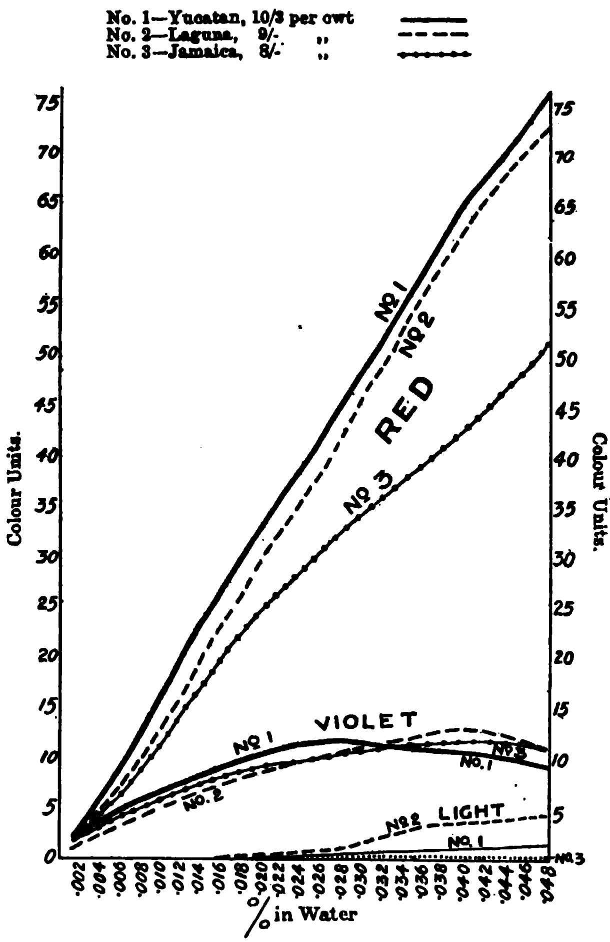
The Lovibond tintometer is in use by silk, wool, and cotton dyers for testing the colour value of dyestuffs and comparing their relative action on different yarns, cloths, etc., and estimating the value of waste liquors. The fastness of colours against light, soap, acids and alkalies can be determined and registered; and to a certain extent shades can be built up by its aid. It is also of use in determining the colour value of tannin extracts used in the weighting of silk, or dyeing of cotton. It is of value in testing the colour of oil, soaps, and also for registering the shade of lakes during the process of manufacture and in the finished state.

The following sets of curves as originally published by Mr. Lovibond will illustrate its use diagrammatically.

A considerable number of the colouring matters of commerce, possessing definite names, are mixtures of two or more dyes. Mechanical mixtures may usually be recognised by sprinkling the dye powder on a piece of filter-paper and then floating the latter on water or alcohol contained in a plate or flat basin. Stains appear on the paper, and if the dye is of a simple character, these are all of the same colour. On the other hand, if a mixture be under examination, the dye particles dissolve with their respective colours, and the paper appears of two or more tints, according to the number of different

colouring matters in the mixture. This appearance becomes very marked when the wet paper is held up to the light. It is even possible

SPECIFIC ABSORPTION CURVES OF THREE COMMERCIAL SAMPLES OF LOGWOOD.

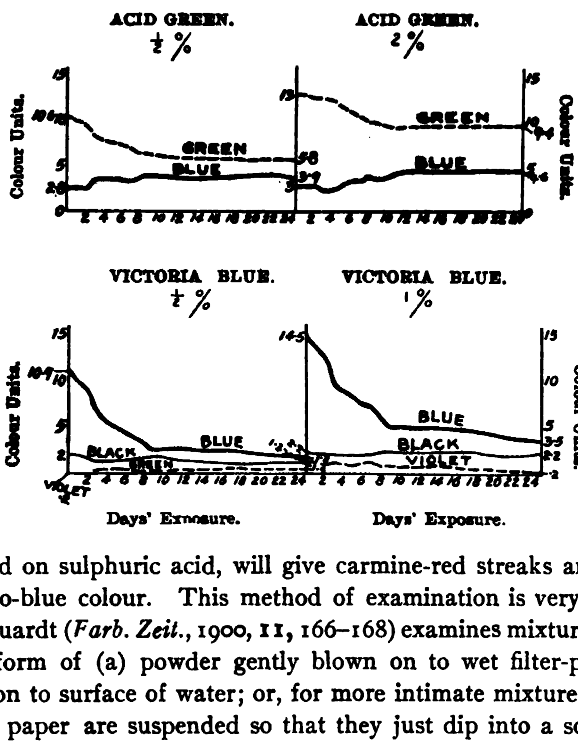


in this way to form an approximate idea of the relative proportions of the constituents of a mixture.[1]

[1] This is sometimes of importance when it is desired to examine dyes "ordered to shade." Thus many cheap violets contain magenta.

With mixtures of azo dyes, the constituents of which are too similar in shade to be recognised when dissolved side by side on filter-paper, the powdered dye may be sprinkled sparingly on the surface of pure, concentrated sulphuric acid contained in a porcelain dish. In many instances the particles will dissolve with marked differences in colour. Thus a mixture of Orange II (Mandarin) with Croceïn Scarlet, when

FADING CURVES OF ANILINE DYES ON WOOL EXPOSED TO DIRECT SOUTH DAYLIGHT.



sprinkled on sulphuric acid, will give carmine-red streaks and others of indigo-blue colour. This method of examination is very sensitive

Marquardt (*Farb. Zeit.*, 1900, **11**, 166–168) examines mixtures of dyes in the form of (a) powder gently blown on to wet filter-paper, (b) dusted on to surface of water; or, for more intimate mixtures, slips of blotting paper are suspended so that they just dip into a solution of the dye. The different colours rise at varying rates by capillary action.

Capillary Separation of Colouring Matters.

Another method of examining certain mixed dyestuffs consists in dissolving the sample in the smallest possible quantity of alcohol,

diluting the solution with rather more than its own volume of water, and then dropping the liquid on a piece of filter-paper, when concentric circles of different tones of colour will be produced if a mixture be under examination. Magenta has been examined in this way for Violaniline, Mauvaniline, or Chrysaniline, and the same method may be employed for testing aniline blues and violets.

The test is not reliable when the colours in a mixture possess the same, or nearly the same capillarity.

A more delicate application of capillary attraction is that of F. Goppelsroeder (*J. Soc. Dyers and Col.*, 1888, **4**, 5), who suspends a number of strips of Swedish filter-paper in such a manner that the lower ends of the strips dip into a series of small beakers containing solutions of the dyes to be tested. The solvent rises to a greater height than the colouring matter. Picric acid stands next to water in capillarity, and if the method be applied to a mixed solution of picric acid and turmeric, after a time three zones or layers may be distinguished. The highest narrow zone is produced by water only; below this there is a broad yellow zone containing picric acid; while in the lowest zone only the colouring matter of turmeric exists. If the lowest zone is cut off, the colouring matter dissolved off with alcohol, and the process repeated with the solution obtained, the picric acid zone will be observed to be very narrow and faintly coloured. Interesting results are obtained when indigo extract is examined in a simple manner. Traces of rosaniline may be detected in magenta by the same means. When an alcoholic solution of Azuline was examined by the capillary test three coloured zones are produced, namely, pink, violet, and blue. In the alcoholic solution of the blue zone, silk was dyed a much purer blue than by the original colouring matter.

Patterson gives the following results of the "capillary speeds" of some well-known aniline colours:

The numbers corresponding to each colour represent its capillary speed in millimetres per minute. The method employed for obtaining these results was as follows: Strips of pure, dry bibulous paper, measuring about 7.5 cm. long by 4 cm. broad, were prepared. Then a measured quantity (7.5 c.c.) of the colour solution under examination, made with cold distilled water, was introduced into a beaker. The depth of this solution measured exactly 5 mm. The end of one of these bibulous strips was then dropped to the bottom of the

solution in the beaker, and the capillary ascent of the colour was accurately noted after one minute.

Taking water as 100 the following results were obtained, arranged according to their relative capillary speeds:

Water	100	Acid Violet	57.1
Acid Magenta	100	Eosin	57.1
Acid Green	100	Alkali Blue	50.0
Naphthol Green	100	Rhodamine	42.8
Orange G	92.8	Tropæolin OOO	42.8
Fast Yellow	92.8	Malachite Green	35.7
Picric acid	85.7	Brilliant Green	28.5
Naphthol Yellow S	82.1	Methyl Violet	14.2
Uranin	78.5	Magenta	14.2
Tropæolin O	71.4	Phenylene Brown	14.2

Mechanical mixtures of dyes are common; more intimate mixtures are sometimes produced by co-precipitation, or evaporation of a mixed solution. In almost all such cases one of the constituents of the mixture possesses a greater affinity for fibres than the other, and it is this circumstance which forms the principal disadvantage of such mixtures in practice. If a dye-bath be made up with the colouring matter, and small samples of wool or silk dyed successively therein until the bath is exhausted, the colouring matter, if simple, will give a shading down from one and the same colour. But in the case of a mixture each consecutive sample will have a different shade, and the first and last samples will be entirely different in colour. The division obtained in this way is often a very sharp one, and it becomes easy to recognise impurities in colour whether due to accident or intention. The test can be conveniently conducted in a wide test-tube or small beaker, wool yarn being the fibre used to withdraw the dye from the bath.

II. Chemical Investigation of Dyestuffs.

Several other systematic methods have been described for recognising the various commercial colouring matters. These schemes have generally the defect of describing the colouring matters merely by their commercial names, and of being based merely on certain colour-tests. Bearing in mind the great number of dyes now met with in commerce, and the rapidity with which they disappear and may be replaced by new colours, and old ones under new names, no complete scheme of examination can be looked for. E. Weingärtner (*J. Soc.*

Dyers, and Col., 1887, 3, 67), classified artificial colouring matters into 3 classes: I. Basic colouring matters soluble in water; II. Acid colouring matters soluble in water; and III. Colouring matters insoluble in water.[1]

The soluble basic colouring matters are distinguished from the acid dyes by a reagent prepared by dissolving 25 grm. of tannin and an equal weight of sodium acetate in 250 c.c. of water. This precipitates the basic dyes only. A few drops of the reagent are added to a 1–2% aqueous solution of the dye, and if any precipitation occurs the liquid is heated, as certain sulphonated derivatives of triphenylmethane give precipitates at first which redissolve at a higher temperature.

Weingärtner's tables for the recognition of artificial colouring matters are given below. The group to which the dyestuff belongs having been ascertained, the colouring matter may usually be identified by its special reactions. The reducing agent used being zinc dust.

Observations.—After having reduced the basic colouring matter with zinc powder and hydrochloric acid, the liquid should be filtered rapidly. It is very important to neutralise the filtered liquid with sodium acetate, since hydrochloric acid in excess may form with the basic colour acid salts of different colour from the neutral salts.

The original shade does not appear on oxidation with the colouring matters in column F, but in certain cases oxidation produces shades dif-

[1] The following table shows the solubility of certain coal-tar dyes in water and alcohol, as determined by A. Brunner (*J. Soc. Dyers*, 1887, 3, 194):

Colouring matters	Amount dissolved by 100 parts of	
	Water	Alcohol
Aurin	almost insoluble	40
Bismarck Brown	3	0.35
Corallin	2	0.5
Dahlia Blue	4	1
Eosin	2	1
Ethyl Orange	0.02	almost insoluble
Gentian Violet	1.5	3
Luteolin	0.28	0.6
Magenta	0.3	10
Malachite Green	4	5
Manchester Yellow	2	0.15
Methylene Blue	3	0.15
Methyl Green	7	0.25
Methyl Violet	2	1.5
Safranine	0.6	0.4
Tropæolin OO	0.05	0.1
Vesuvine	2	0.2

Table I.—*Artificial Colouring Matters Soluble in Water. Basic Colouring Matters.*

<table>
<tr><td colspan="6">The aqueous solution gives a precipitate with the tannin reagent. The aqueous solution is heated with zinc powder and hydrochloric acid, and filtered rapidly. If the decolourised liquid does not reoxidise on the filter, the filtrate is treated with sodium acetate and then well shaken with air.</td></tr>
<tr><td colspan="5">The original shade reappears.[1]</td><td rowspan="2">The original shade does not reappear</td></tr>
<tr><td>Red</td><td>Yellow or orange</td><td>Green</td><td>Blue</td><td>Violet</td></tr>
<tr><td>Magenta.
Tolylene Red.
Safranines.</td><td>Phosphine.
Flavaniline.</td><td>Malachite Green.
Brilliant Green.
Methyl Green</td><td>Methylene Blue.
New Blue.
Muscarine.</td><td>Methyl Violet.
Hofman's Violet.
Mauveine.
Amethyst.
Crystal Violet.</td><td>Chrysoïdine.
Vesuvine.
Auramine.
Victoria Blue.
Methylene Green (see below).</td></tr>
<tr><td>A</td><td>B</td><td>C</td><td>D</td><td>E</td><td>F</td></tr>
</table>

Table II.—*Artificial Colouring Matters Soluble in Water. Acid Colouring Matters.*

<table>
<tr><td colspan="6">The aqueous solution does not give a precipitate with the tannin reagent. The aqueous solution is heated with zinc powder and hydrochloric acid, and filtered rapidly. If the decolourised liquid does not reoxidise on the filter, the filtrate is treated with sodium acetate and then well shaken with air.</td></tr>
<tr><td colspan="5">The solution is decolourised.</td><td rowspan="2">The solution becomes brownish-red. The colour of the ammoniacal solution reappears on the paper.</td></tr>
<tr><td colspan="2">The original colour reappears on paper.</td><td colspan="3">The original colour does not appear.</td></tr>
<tr><td colspan="2">The aqueous solution is acidified with hydrochloric acid, and treated with ether.</td><td colspan="3">The colouring matter is heated on platinum foil.</td><td rowspan="4">Alizarin S.
Alizarin Blue S.
Cœruleïn S.</td></tr>
<tr><td>The ether dissolves the colouring matter, and the solution immediately becomes colourless.</td><td>The ether remains colourless.</td><td>It deflagrates without formation of coloured vapours.</td><td colspan="2">Burns quietly, or slightly deflagrates, giving off coloured vapors.
Heat a piece of cotton cloth, not mordanted, in the aqueous solution.</td></tr>
<tr><td rowspan="2">Phthaleïns.
Eosins.
Aurin.</td><td rowspan="2">Sulphonated rosanilines.
Sulphonated indulines.</td><td rowspan="2">Nitro-colouring matters.</td><td>The colouration of the dye is fast to warm soaping.</td><td>The colour does not resist warm soaping.</td></tr>
<tr><td>Azo-colours from benzidine, etc.</td><td>Azo-colours.
Tartrazin.
Erythrosin.</td></tr>
<tr><td>G</td><td>H</td><td>I</td><td>J</td><td>K</td><td>L</td></tr>
</table>

[1] In many of these cases the use of an oxidising reagent has been found to be necessary.

fering from the original. When Bismarck Brown (vesuvine) and chrysoïdine are reduced, the di- and tri-amines are formed, which easily oxidise in the air with brownish-red colour. It is very important to distinguish this shade form the original, which is brown or yellow. After reduction and oxidation Methylene-green gives a blue shade.

The oxidation of the reduced solution on the filter-paper may be facilitated by gently heating. Some colours reoxidise with such rapidity that the original colour returns while filtering.

Methylene Green forms a dark green aqueous solution, which becomes quite colourless on reduction, but passes into sky-blue in presence of air. The solid dye substance dissolves in strong sulphuric acid with dark green colour.

Observations.—*a.* The reduction of the acid yellow, orange, ponceau, and claret non-fluorescent colours requires special precautions. The best way is to treat with zinc powder and hydrochloric acid, and afterwards to neutralise with sodium acetate, as has already been pointed out. The reduction will often be too slow if ammonia or acetic acid be used.

b. It is necessary, as before, to compare with great care the original colour with that which is produced by reoxidation, so that their identity or difference may be not mistaken. In the reduction of nitro- or azo-bodies, diamines or amino-phenols are formed, which on oxidation give dirty or brown shades. In the column K this remark equally applies to erythrosin, for when that colouring matter is reduced, iodine is separated and fluorescin formed.

c. All the colouring matters not specified in *a* are reduced by zinc and ammonia.

d. When the acid colours are being reduced, the solution, as long as zinc-powder is present, should be colourless, or at most slightly yellow or red.

e. The nitro-derivatives of the azo-colouring matters and of fluoresceïn can be easily recognised by the formation of "Pharaoh's serpents" on heating a small quantity (0.5 grm.) on platinum foil.

f. In order to find the group NO_2 with certainty in a yellow colouring matter (*e. g.*, picric acid), it is necessary to add a little sodium carbonate.

g. It is very difficult completely to reduce Alizarin S. It is therefore entered in column L. The colour of the ammoniacal solution more often returns, but if the reduction has been carried too far it does not reappear.

Table III.—*Artificial Colouring Matters Insoluble in Water.*

The colouring matter is treated with water, and a little 5% solution of sodium hydroxide added.

<table>
<tr><td colspan="2">The colouring matter dissolves.</td><td colspan="5" rowspan="2">The colouring matter does not dissolve. It is heated with 70% alcohol.</td></tr>
<tr><td colspan="2">The alkaline solution is filtered, treated hot with zinc-powder, and then poured on a filter-paper.</td></tr>
<tr><td rowspan="2">The colour of the alkaline solution reappears.</td><td rowspan="2">The colour of the alkaline solution does not reappear, or the solution changes colour during the reduction, the new colour being permanent.</td><td colspan="4">It is dissolved.</td><td>It is not dissolved.</td></tr>
<tr><td colspan="2">The alcoholic solution is not fluorescent. Add a little 33% sodium hydroxide solution.</td><td colspan="2">The alcoholic solution is fluorescent. Add a little 33% sodium hydroxide solution.</td><td rowspan="3">Indigo.[1]</td></tr>
<tr><td rowspan="2">Cœrulein (in paste).
Gallein
Gallocyanin.
Galloflavin.</td><td rowspan="2">Canarin.
Alizarin.
Anthrapurpurin.
Flavopurpurin.
Nitroalizarin.
Alizarin Blue.
Chrysamin.
Solid green.</td><td>The colour changes to red-brown.</td><td>The colour does not change.</td><td>The fluorescence disappears.</td><td>The fluorescence persists.</td></tr>
<tr><td>Indulines.
Nigrosines.
Rosaniline Blue.
Diphenylamine Blue.</td><td>Indophenol.</td><td>Magdala Red.</td><td>Primrose, Cyanosin.</td></tr>
<tr><td>M</td><td>N</td><td>O</td><td>P</td><td>Q</td><td>R</td><td>S</td></tr>
</table>

O. N. Witt (*J. Soc. Dyers and Col.*, 1886, **2**, 64; has given the following tables which may be of value in special cases:

[1] Indanthrene dyestuffs are soluble in alkaline reducing agents such as an alkaline solution of sodium hydrosulphite from which they dye unmordanted cotton.

RED COLOURS.

	Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol and ether	Zinc powder	General remarks
I.—Insoluble in cold water, almost or quite insoluble in hot water, Easily soluble in alcohol.	*Carminaphtha.*	......	......	Reddish-violet.	Solution in alcohol salmon red, without any fluorescence.	......	This dye is not much known; it is manufactured by L. Durand and Huguenin, and has been used to a small extent in calico printing.
	Magdala Red. (Naphthalene Rose.)	......	......	Greenish-gray, turning red on dilution with water. A reddish-violet precipitate forms afterwards.	Solution in alcohol, bluish-red with intense orange-red fluorescence	......	Spectroscope shows a broad absorption band, which completely extinguishes the yellow and green of the spectrum.
	Quinoline Red.	Insoluble in cold, rather easily soluble in hot water.	......	Colourless; on dilution, every drop of water produces an intense red, which disappears on stirring. On diluting sufficiently, the whole is coloured deep magenta.	As with Magdala-red.	......	Spectroscope shows absorption band rather more to the right, so that some of the yellow remains. The reaction with H_2SO_4 differs entirely from that in case of Magdala-red. The property of yielding colourless solution with concentrated H_2SO_4, which becomes coloured dilution, is a characteristic reaction of several quinoline dyes, and does not occur with dyes of other classes.
	Eosins. Soluble in alcohol.	......	......	Lemon-yellow to orange. No striking change of colour on dilution.	Solution in alcohol is fluorescent likewise, but the fluorescence is greener.	......	The different eosins may be distinguished by the shades they give when small samples are dyed.
	Rhodindins. (Indulines of the Napthalene series.)	......	......	Green, turning bluish-red on dilution.	Solution in alcohol, dull bluish-red.	......	......

RED COLOURS.—*Continued.*

		Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol and ether	Zinc powder	General remarks
II.—The dye is more or less soluble in cold water, copiously in boiling water.	(*a*) Precipitated by sodium hydroxide. *Basic dyes.*	*Fuchsine.* (Rubin, Magenta, Aniline Red.)	Bluish-red.	Solution in water is turned yellowish-brown by HCl or H_2SO_4, but the red colour is restored by sodium acetate.	Dissolves with a yellowish-brown colour.	....	Solution in water permanently decolourised.	In a dilute solution, to which ammonia has been added, and which is only pale red, wool is dyed a deep red on boiling. The sample either consists of distinct green crystals or of a metallic-green powder.
		Toluylene red. (Neutral red.)	Bluish-red.	Ammonia precipitates orange-coloured flakes, which are dissolved by ether to a red solution with yellow fluorescence.	Green, changing on dilution through blue and violet to red.	....	....	The product is generally very impure, and will give these reactions with dirty colours.
	(*b*) Not precipitated by sodium hydroxide. Acid dyes or basic dyes of the saffranine class.	*Gallein.*	....	On addition of sodium hydroxide to the solution in water, the colour changes to intense blue.	Brownish-yellow somewhat redder on dilution.			
		Safranine and Safranisol.	....	Addition of alcohol to the solution in water causes a distinct greyish-yellow fluorescence, not precipitated by addition of acids.	Green changing on dilution through blue to red.	....	Decolourised, but the original colour is immediately restored on admission of air.	Distinguish these two products by the shade given in dyeing.
		Eosin.	Pure red, with a greenish yellow fluorescence, which becomes all the more distinct as more water is added.	Acids precipitate orange-yellow flakes, which are soluble in ether.	Pure yellow.	Solution in ether pure yellow without fluorescence.		

RED COLOURS.—*Continued.*

	Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol and ether	Zinc powder	General remarks
II.—The dye is more or less soluble in cold water, plentifully in boiling water. (*b*) Not precipitated by sodium hydroxide. Acid dyes or basic dyes of the safranine class.	*Eosin Scarlet.* (Bromonitro-fluorescein.)	Of a more bluish-red than with eosin, and is without any fluorescence.	Acids give a straw-yellow precipitate.	Golden-yellow.	Solution in ether straw-yellow.	Zinc powder decolourises a solution which has been treated with ammonia. On sprinkling the decolourised solution upon blotting paper it is turned an intense blue by the action of the air. (Distinction from Eosin.)	
	Phloxin. *Rose Bengale.*	Bluish-red without fluorescence.	Acids give an orange-yellow precipitate, which is soluble in ether.	Orange-yellow.	....	Zinc powder and ammonia decolourise but the colour does not return, or but very slightly on admission of air.	Distinguish these two products by the shade.
	Biebrich Scarlet. (Double Scarlet.)	The concentrated solution in hot water stiffens on cooling to a jelly.	Acids give a brown flaky precipitate.	Grass-green; gives on dilution, first a blue colour, and then a dirty brown precipitate.	....	On warming with zinc powder and ammonia, the solution is turned first pure yellow and then colourless.	

RED COLOURS.—*Continued.*

II.—The dye is more or less soluble in cold water, plentifully in boiling water.

(*b*) Not precipitated by sodium hydroxide. Acid dyes or basic dyes of the saffranine class.

Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol and ether	Zinc powder	General remarks
Crocein Scarlet 3 B.	Indigo blue changing on dilution through violet into red.	Barium chloride added to a solution in water gives a flaky red precipitate, which on boiling becomes suddenly crystalline and deep violet-black.				
Congo Red.	If cotton is boiled in the aqueous solution, with or without a small addition of soap, it is dyed a red colour, which will stand washing.	The slightest trace of acid added to a solution in water changes it to a pure blue.	Slate-blue, no change on dilution.			
Xylidine Ponceau.	The solution in hot water stiffens on cooling, with separation of bronze-colored shining crystals.	....	Violet; brown precipitate on dilution.	....	....	
Crocein Scarlet. 7 B. Extra.	....	Concentrated solution in water, treated with magnesium sulphate, yields on cooling, long silky needles of the magnesium salt.	Violet.	....	....	Dyes wool a beautiful scarlet-red. This dye is produced by the action of diazonaphthionic acid upon the crocein-beta-naphtholsulphonic acid.

RED COLOURS.—*Concluded.*

II.—The dye is more or less soluble in cold water, plentifully in boiling water.

(*b*) Not precipitated by sodium hydroxide. Acid dyes or basic dyes of the saffranine class.

Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol and ether	Zinc powder	General remarks
Ponceau R., 2 R., 3 R. Anisol Red. Coccin.	....	Calcium chloride and barium chloride give an amorphous flaky precipitate from the solution in water.	Pure rose-coloured or carmine red; on dilution a brownish-red precipitation.	....	....	These colours, from beta-naphtholdisulphonic acids, may be distinguished by the shade given in dyeing.
Acid Aso Rubin.	....	An addition of calcium chloride to a solution in water, gives a red flaky crystalline precipitation.	Bluish - violet; red on dilution.	....	....	Dyes wool a magenta red.
Fast Red. (Rocelline.)	Deep brownish-red.	The addition of a drop of saturated sodium carbonate solution to a concentrated boiling solution of the dye in water, precipitates the sodium salt of the dye in the form of sparkling brown scales.	Blue; on dilution a yellowish-brown precipitate.	....	....	Dyes wool a deep brownish-red.
Bordeaux B.	Claret red.	Calcium chloride and barium chloride give flocculent amorphous precipitates.	Indigo blue.	....	....	
Acid Magenta.	Fine blue-red.	The solution in water is completely decolourised by sodium hydroxide, but the original colour is restored by acetic acid.				

GREEN COLOURS.

Name	Solution in water	Reactions, etc.	Solution in concentrated H_2SO_4	General remarks
Cærulein.	But slightly soluble in water, with olive-brown colour.	On addition of an alkali, plentiful solution with grass-green colour.	Dirty-brown colour.	
Victoria Green. *Brilliant Green.*	Easily soluble, with beautiful green colour.	Alkalies produce a rose-coloured or grey precipitate; strong acids colour solution yellow.	Yellow.	Distinguished by the shade obtained in dyeing.
Iodine Green. *Methyl Green.*	Easily soluble, with beautiful blue-green colour.	Acids impart a yellow colour; alkalies decolourise without a trace of precipitation.	Yellow.	A dyed sample, on being heated above 100°, is turned violet. Methyl green dyes in a neutral bath.
Greens from the sulphonic acids of benzaldehyde. Malachite Green, Light Green, S. (cerumn) Acid Green, Helvetia Green.	Easily soluble, with a proportionately weak green colour.	Acids first intensify the colour and on further addition turn to a yellow; alkalies decolourise completely.	Yellow.	Silk and wool (the latter after treatment with sulphuric acid) can only be dyed in an acid bath (distinction from Methyl Green). Dyed samples will sustain a heat of 150° for a short time without damage.

VIOLET COLOURS.

Name	Solution in water	Reactions, etc.	Solution in concentrated H_2SO_4	General remarks
Regina Purple (Diphenylrosaniline.)	Sparingly soluble.	....	Cinnamon brown.	Soluble in alcohol.
Methyl Violet, R—6 B. *Hofmann's Violet.*	Easily soluble.	Alkalies give a precipitate, hydrochloric acid imparts first a green and then a yellow colour.	....	Distinguished by the shades.
Mauvein. (Perkin's Violet, Rosolane.)	Not very easily soluble.	Alkalies effect a violet precipitation.	Grey colour, on dilution successively greyish-green, sky-blue, bluish-violet, red-violet.	
Lauth's Violet. (Thionine.)	Soluble.	Acids give a pure blue precipitate, alkalies a red-violet one.	Emerald-green, on dilution sky-blue.	Zinc powder in acid as well as ammoniacal solution forms a splendid vat.
Gallocyanin.	Soluble on boiling.	Hydrochloric acid imparts a pure carmine-red colour.	Blue colour, redder on dilution.	
Amethyst. *Fuchsia.* *Girofle.*	Solution; red-violet.	Addition of alcohol produces a carmine-red fluorescence.	Emerald-green colour, on dilution blue or violet.	Violet saffranine colours; ethylated and methylated homologues of phenol saffranine.

The foregoing collection includes most of the dyes which were then in the trade.

BLUE COLOURS.

Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol	Zinc powder	General remarks
Rosaniline Blue. Diphenylamine Blue.	Quite insoluble.	Hydrochloric acid leaves the solution in alcohol unchanged, but for the precipitation of microscopic shining green crystals; sodium hydroxide changes colours to brownish-red.	Light-red brown.	Dissolves with a blue colour of varying shade.	....	Distinguished by dyeing on silk, and especially on comparing by artificial light.
Indophenol.	Insoluble.	The solution in alcohol is coloured red by hydrochloric acid, but is unchanged by alkalies.	....	Soluble.		
Methylene Blue.	Easily soluble.	Hydrochloric acid gives a greenish precipitate; sodium hydroxide a violet-red precipitate.	....	....	Reduced by zinc powder, the colour being restored on access of air.	Contains zinc.
Victoria Blue.	Rather easily soluble.	Acids impart a yellowish-brown colour; alkalies form a red-brown precipitate.				
Alkali Blues. R−6 B. (Nicholson's Blues.)	Easily soluble.	Alkalies decolourise almost completely.	....	....	....	Distinguish by the shade. Wool attracts the dye from the alkaline solution, and after washing with water a deep blue colour is developed by dilute acids.
Water Blues. R−6 B.	Easily soluble.	Alkalies do not form a precipitate in the aqueous solution.	....	....	Decolourise permanently.	Wool is dyed in an acid solution.
Indigo Carmine. (Indigo extract.)	Easily soluble.	Dilute nitric acid decolourises permanently on boiling.	....	....	Zinc powder and ammonia form a vat—*i. e.*, the colour is restored on access of air.	Only dyed in an acid bath.
Indulines. R−6 B.	Insoluble.	Solution in alcohol is coloured brownish-red to violet by alkalies.	Blue colour.	Soluble.	....	The more soluble, the redder the shade.

BLUE COLOURS.—*Concluded.*

Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol	Zinc powder	General remarks
Indulines soluble in water.	Soluble.	Acids form a blue precipitate; alkalies a red to violet colouration; dilute nitric acid does not decolourise even on warming.	....	....	Zinc powder and ammonia forms a vat.	Distinguished by the shade.
Leucindophenol.	....	Sodium hydroxide imparts a blue colour immediately on access of air.	....	....	....	The commercial product gives a grey paste.
Orthonitrophenylpropiolic acid.	....	Soluble on addition of sodium hydroxide without formation of blue colour.	....	....	....	The commercial product forms a grey paste. An addition of grape-sugar and boiling gives rise to the separation of indigo blue in crystals.

YELLOW AND ORANGE-RED COLOURS.

	Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol	General remarks
I.—The dye is insoluble in cold water, likewise in hot water, or but difficulty soluble. Soluble in alcohol.	*Quinaphthalene.*	....	Solution is not affected by acids or alkalies; at most the colour is rather deepened.	....	Lemon yellow.	
	Turmeric dye.	....	Solution is left unchanged by acids; alkalies and boracic acid turn the same a deep brown-red.	....	Golden yellow.	
	Dimethylaminoazobenzene.	....	Hydrochloric acid produces a red colouration. In a solution which has been treated with HCl, amyl nitrite produces neither change of colour nor evolution of nitrogen on boiling.	....	Golden yellow.	This colour has been employed to dye artificial wax, prepared from Ozokerit.
	Aminoazobenzene	....	Reaction same as in last-named, except that amyl nitrite produces a change of colour and a weak evolution of nitrogen.	....	Golden yellow.	

YELLOW AND ORANGE-RED COLOURS.—*Continued.*

		Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol	General remarks
II.—The dye is plentifully soluble in water, especially boiling. Dissolves in concentrated sulphuric acid without any intense colouration.	(*a*) No precipitate with sodium hydroxide. *Acid dyes.*	*Picric acid.*	Greenish-yellow; tastes very bitter.	Alkalies turn solution a dark yellow; acids effect no change.			
		Martius' Yellow.	Golden yellow.	Acids form a whitish precipitate.	....	....	See note in introduction.
		Acid Naphthol Yellow.	Golden yellow.	Not precipitated by acids. Potassium chloride causes a crystallisation of needles.			
		Fluorescein. (Uranin.) *Benzylfluorescein.* (Chrysolin.)	Brownish-yellow; a splendid green fluorescence.	Acids cause the fluorescence to disappear, and they also form a precipitate.	....	....	These two dyes can only be distinguished by an exact investigation of the separated dye-acids.
		Quinolin Yellow (Quinaphtalene sulpho acid.)	Golden yellow.	Not precipitated by acids.	....	....	Not decolourised by zinc powder and ammonia, nor by stannous chloride and hydrochloric acid.
	(*b*) Sodium hydroxide gives a precipitate. *Basic dyes.*	*Phosphine.*	....	Yellow; flaky precipitate with alkalies; which is soluble in ether with a pure yellow colour and a splendid green fluorescence.	....	....	The extremely delicate ether test permits of phosphine being recognised in mixtures with grenadine, maroon, etc.
		Flavaniline.	....	Milky-white precipitation by alkalies, which is dissolved again by ether—colourless with a greenish-blue fluorescence.			
		Auramine.	....	Milky-white precipitation by alkalies, which is dissolved again by ether—colourless and without any fluorescence.	....	....	The yellow solution of the dye becomes less intense on boiling with hydrochloric acid, and finally is colourless.

YELLOW AND ORANGE-RED COLOURS.—*Continued.*

		Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol	General remarks
III.—The dye is soluble in water; the solution in sulphuric acid is of an intense colour.—*Azo dyes.*	(*a*) Sodium hydroxide gives a precipitate.	*Chrysoidin.*	Solution of the dye in water forms a blood-red jelly on cooling.	....	Brownish-yellow.	....	Dyes wool yellow.
		Vesuvin. (Bismarck Brown. Phenylene Brown.)	The solution does not gelatinise on cooling.	....	Brown.	....	Dyes wool orange-brown.
	(*b*) Sodium hydroxide gives no precipitate.	*Fast Yellow.*	Yellow.	....	Yellow; salmon-red on dilution.		
		Methyl Orange. Ethyl Orange.	Yellow; crystallises on cooling in glittering gold coloured scales.	Dilute acids give a glittering red-violet precipitate.	Yellow; carmine red on dilution.		
		Tropæolin OO. (Diphenylamine Yellow.)	Yellow; crystallises on cooling.	Calcium chloride and barium chloride give perfectly insoluble precipitates.	Violet; red-violet on dilution with a simultaneous formation of a steel-grey precipitate.		
		Yellow N. (Poirrier.)	Yellow; crystallises on cooling.	Barium chloride precipitates a yellow salt, which crystallises out of excess of water in shining leaflets.	Bluish-green; violet on dilution, with steel-blue precipitation.		

YELLOW AND ORANGE-RED COLOURS.—*Concluded.*

	Name	Solution in water	Reactions	Solution in concentrated H_2SO_4	Solution in alcohol	General remarks
III.—The dye is soluble in water; the solution in sulphuric acid is of an intense colour. *Azo dyes.* (*b*) Sodium hydroxide gives no precipitate.	*Luteolin.*	Yellow; crystallises on cooling.	Calcium chloride gives an orange precipitate, which becomes red and crystalline on boiling.	Yellowish-green; violet on dilution, with a grey precipitate.		
	Citronin. (Jaune indien, Curcumin.)	Yellow; generally dull.	The solution in water is turned deep red to violet on being treated with alcoholic sodium hydroxide.	Carmine-red; yellow on dilution.		
	Orange G.	Orange.	Calcium chloride produces a splendid crystallisation of the calcium salt in leaflets.	Deep orange; no change of colour on dilution.	....	
	Tropæolin O.	Yellow.	Addition of a little hydrochloric acid effects crystallisation in yellow leaflets; addition of more acid, the separation of the free acid in grey needles.	Brownish-orange; no change of colour on dilution.		
	Orange II. (Beta-naphthol Orange, Mandarin.)	Red orange.	Calcium chloride precipitates the beautiful red calcium salt, which crystallises in needles out of an excess of boiling water.	Carmine-red; orange on dilution.		
	Tropæolin OOO. *Orange I.*	Red orange.	Sodium hydroxide turns the solution in water to a carmine-red.	Violet; orange on dilution.		

These earlier analytical tables of Weingärtner and Witt, are necessarily incomplete. Since the publication of these tables a large number of new dyestuffs have appeared, and considerable modifications are necessary, but they may be of value under special conditions and they are therefore given in this volume.

In using these tables certain precautions are necessary and the definition "soluble" and "insoluble" in water is sometimes not satisfactory in practice. The recent and important addition of insoluble azo dyes which are so largely used as lakes must also be remembered. In the case of the zinc dust reaction, derivatives of triphenylmethane are reoxidised by air with great difficulty while the azines, oxazines, thiazines, and acridine colours change with great rapidity on exposure to the air. These triphenylmethane colours are, however, distinguished from those which are broken up instead of forming leuco-compounds by using a stronger oxidising reaction (chromic acid). This grouping into easily and difficultly oxidising reactions is not entirely satisfactory in practice. The quinoline and primuline colours are reduced with great difficulty. The reduction with zinc dust may be conducted as follows: A little of the powder is added to the hot solution of colouring matter and after agitation hydrochloric acid is added drop by drop until the solution is decolourised. An excess of acid must be carefully avoided. It is better to always perform the reduction with ammonia as well as acid. In some cases only the ammonia method will give results.

With some colours the reaction may be carried too far in the presence of acids, and no recovery of colour is then possible. Exposure to air is effected by pouring the reduced solution on to filter-paper and if the colour does not return within 2 minutes the chromic acid solution is applied on the end of a glass rod.

In the case of acid colours and after spotting with chromic acid the spot should be held over a bottle of strong ammonia for some of these colours (eosins, etc.) do not show their true colour when acid. Great care must be taken not to be led astray by secondary colours which may be formed from the diamines and aminophenols obtained by reduction of azo colours.

A. G. Green (*J. Soc. Chem. Ind.*, 1893, **12**, 3), taking Weingärtner's system as a basis, has constructed a scheme of analysis which is given in the following tables. The following group reagents are employed:

1. A solution containing 10% of tannin and 10% of sodium acetate.

GROUP I.—DYESTUFFS SOLUBLE IN WATER.

A.—*Precipitated by Tannin Solution: Basic Colours.*

The aqueous solution is reduced with zinc dust and hydrochloric acid and a drop of the decolourised solution put on filter-paper. If the colour does not quickly return on exposure to air, the spot is touched with a drop of 1% chromic acid solution.

The original colour quickly reappears on exposure to air: *Azine-*, *Oxazine-*, *Thiazine-*, and *acridine colors.*					The colour appears very slowly or not at all on exposure to air, but returns on spotting with 1% chromic acid solution: *Triphenylmethane colours*, and *basic phthaleins.*				The original colour does not return at all.
Red	Orange and yellow	Green	Blue	Violet	Red	Green	Blue	Violet	Yellow and brown
Tolylene red. Safranine. Pyronine. Acridine red.	Phosphine. Benzoflavine. Acridine Yellow. Acridine Orange.	Azine Green.	Methylene Blue. New Methylene Blue N. Thionine Blue. Toluidine Blue. Meldola's Blue. Muscarine. Neutral Blue. Basle Blue R & B B. New Methylene Blue G G. Nile Blue. Capri Blue. Fast Blue. Indazine M. Metaphenylene Blue B. Paraphenylene Blue. Indamines.	Mauve. Amethyst. Neutral Violet. Fast Neutral Violet. Prune. Paraphenylene Violet. Indamines.	Magenta. Isorubine. Rhodamine[1]	Malachite Green. Brilliant Green. Methyl Green. Iodine Green.	Victoria Blue B.[2] Victoria Blue 4 R. Night Blue.	Methyl Violet. Crystal Violet. Hofmann Violet. Benzyl Violet. Ethyl Purple. Regina Purple.	Auramine.[3] Thioflavine T.[4] Chrysoidin. Bismarck Brown.

[1] The colour returns more quickly than with the rosanilines.
[2] The shade which returns is much greener than the original.
[3] The reduced solution gives a beautiful violet when the spot on filter-paper is warmed over a flame till dry.
[4] Is only reduced with difficulty and very slowly.

GROUP I.—DYESTUFFS SOLUBLE IN WATER.—*Continued.*

B.—*Not Precipitated by Tannin Solution: Acid Colours.*

The aqueous solution is reduced with zinc dust and hydrochloric acid, or with zinc dust and ammonia, and a drop of the decolourised solution is put on filter-paper. If the colour does not quickly return on exposure to air, the spot is touched with a drop of chromic acid solution (1% CrO_3+5% H_2SO_4), warmed over a flame, and then held in the vapour of ammonia.

<table>
<tr><td colspan="6">The solution is decolourised</td><td rowspan="2">Not decolourised (by zinc and ammonia), but changed to brownish-red. Original colour returns quickly on exposure to air.</td><td rowspan="2">Very slowly and incompletely decolourised (zinc and ammonia).</td><td rowspan="2">Not altered by zinc and ammonia; very slowly or not at all by zinc and hydrochloric acid.</td></tr>
<tr><td>The original colour quickly reappears on exposure to air.</td><td colspan="2">The original colour does not reappear on exposure to air, or only very slowly, but returns with chromic acid, and exposure to ammonia vapour.</td><td colspan="3">The original colour does not return at all: Azo-, nitro-, nitroso-, and hydrazine colours.</td></tr>
<tr><td rowspan="5">Sulphonated azines, oxazines, thiazines, etc.:—
Soluble indulines.[1]
Soluble nigrosines.[1]
Resorcin blue.
Azurine.
Thiocarmine.
Basle blue R S and B B S.
Gallamine blue.
Gallocyanine.
Gallanilic indigo P S.
Indigo-carmine.
Saffrosin.
Azo carmine.
Mikado Orange.[1]
Sulphide dyestuffs.</td><td colspan="2">The aqueous solution of the dyestuff is acidified and shaken with ether.</td><td colspan="3">Heated on platinum foil.</td><td rowspan="5">Alizarin S.
Alizarin Blue S.
Cœrulin S.</td><td rowspan="5">Clayton Yellow.
Thiazole Yellow.
Turmerine.
Mimosa.</td><td rowspan="5">Quinoline Yellow S.
Primuline.
Thioflavine S.
Oxyphenine.</td></tr>
<tr><td rowspan="4">The ether extracts the colour-acid, leaving the solution nearly colourless:
Phthaleins and aurine:—
Uranin.
Chrysolin.
Eosin.
Erythrin.
Phloxin.
Erythrosin.[2]
Rose bengale.[2]
Cyclamin.
Aurin.
Corallin.</td><td rowspan="4">The ether remains colourless:
Sulphonated triphenylmethane colours:—
Acid Magenta.
Acid Violets.
Formyl Violet.
Alkali Blues
Soluble Blues.
Patent Blue.
Fast Green, bluish.
Acid Greens.
Guinea Green.
Chrome Violet.</td><td rowspan="4">Deflagrates with production of coloured vapors:
Nitro-colours:—
Picric acid.
Victoria Yellow.
Aurantia.
Martius Yellow.
Naphthol Yellow S.
Brilliant Yellow.
Aurotin.</td><td colspan="2">Burns quietly or deflagrates slightly, giving off coloured vapours:—Azo-, nitroso-, and hydrazine colours.</td></tr>
<tr><td colspan="2">The colour dyed upon unmordanted cotton.</td></tr>
<tr><td>Resists warm soap.</td><td>Is stripped by warm soap.</td></tr>
<tr><td>Substantive Azo-colours.</td><td>Ordinary azo-colours.
Naphthol Green B.
Tartrazin.</td></tr>
</table>

[1] If the reduction is carried too far, the colour does not return. [2] Iodine is separated by the chromic acid, but disappears on exposure to ammonia.

GROUP II.—DYESTUFFS INSOLUBLE IN WATER.

The powder or paste is treated with water and a few drops of 5% sodium hydroxide solution.

The colour dissolves		The colour remains insoluble				
The alkaline solution is heated with zinc dust and ammonia, and a drop is put on filter-paper.		Soluble in 70% alcohol				Insoluble in 70% alcohol
		Solution not fluorescent		Solution fluorescent		Indigo. Aniline Black. Primuline base.
Decolourised or changed to light-brown. The original colour returns very quickly on exposure to air.	Decolourised or changed to brown. The original colour does not reappear on exposure to air.	On adding sodium hydroxide (33%) to the alcoholic solution		On adding sodium hydroxide (33%) to the alcoholic solution		
		Colour becomes reddish-brown.	Colour not altered.	Fluorescence destroyed.	Fluorescence remains.	
Cœrulein. Gallein. Gallocyanin. Gallanilic Violet B S. Gallanilic blue P. Galloflavin. Alizarin blue. Alizarin black. Alizarin cyanine. Rufigallol.	Alizarin. Anthropurpurin. Flavopurpurin. Alizarin Orange. Alizarin Brown. Alizarin Bordeaux. Alizarin Yellow G G and R. Chrysamin. Soudan Brown. Patent Fustin. Myrtle. Gambin R and Y Dioxine.	Induline. Nigrosine. Rosaniline Blue. Diphenylamine Blue.	Indophenol. Soudan II and III. Carminaphtha.	Magdala Red.	Spirit Eosins. Cyanosin.	

2. Zinc dust and dilute hydrochloric acid, or zinc dust and aqueous ammonia.

3. Solution containing 1% of chromic acid (for basic colours).

4. Solution containing 1% of chromic acid or potassium dichromate and 5% of sulphuric acid (for acid colours).

The members of the same group are distinguished from each other by their behaviour toward aqueous acids and alkalies, concentrated sulphuric acid, alcohol, etc., and by their dyeing properties. (See the reactions of the various colours as given by Witt, Weingärtner, and others.)

A.G.Rota(*Chem. Zeit.*,1898,22,437) gives a systematic scheme for the analysis of dyestuffs, based on the chemical constitution of the dyestuff. In accordance with the views of Nietzki and Armstrong, the organic dyestuffs are regarded as quinone derivatives; those having the structure of mono- and di-aminoquinones are capable of reduction by stannous chloride, while those in which the oxygen atom of the quinone is replaced by a divalent hydrocarbon group are not reduced. Thus, regarding $O=R=O$ as representing an ortho- or paraquinone, the nitro-, azo-, and iminoquinone dyestuffs represented by $O=R=N-$ or $-N=R=R-$ are reducible, but the oxyquinone and triphenylmethane dyestuffs having the composition $O=R=C=$ and $-N=R=C=$ are not reducible by this reagent.

The reduced colouring matters can be subdivided into two groups, according to whether the colour is restored on oxidation with ferric chloride; and the unreduced colouring matters can also be subdivided according to their behaviour on treatment with potassium hydroxide.

The reduction is carried out in an aqueous or alcoholic solution of the dyestuff diluted to about 1 : 10,000. Of this solution 5 c.c. are treated with 4–5 drops of concentrated hydrochloric acid and the same amount of a 10% solution of stannous chloride. The mixture is shaken, and, if necessary, heated to the boiling point. Is not entirely decolourised, the solution should be diluted still further and more stannous chloride added.

Sulphide dyestuffs may be detected by the evolution of hydrogen sulphide to which they give rise on reduction with stannous chloride and hydrochloric acid or an acid solution of titanous chloride: The hydrogen sulphide is tested for in the usual manner by the darkening which it produces on paper moistened with an alkaline lead acetate solution; the reagents should be tested for freedom from sulphur and

account must be taken of other compounds containing sulphur which might react similarly. All sulphide dyestuffs are precipitated from aqueous solution by mineral acids. Indanthrene and other newer vat dyestuffs resemble indigo in being soluble in a solution of alkaline sodium hydrosulphite; they then form highly coloured solutions which dye unmordanted cotton. They are insoluble in water, in dilute acids, and in alkalies.

By means of these tables the group to which a dyestuff belongs may be determined and be further identified by recourse to a table of reactions for the particular group in question.

TABLE A.

GENERAL CLASSIFICATION OF ORGANIC COLOURING MATTERS.

A portion of the aqueous of diluted alcoholic solution treated with HCl and $SnCl_2$.

<table>
<tr><td colspan="2">Complete decolourisation.[1] Reducible colouring matters.
The colourless solution after neutralisation with KOH is treated with Fe_2Cl_6, or shaken and exposed to the air.</td><td colspan="2">The colour is changed no further than with HCl alone. Non-reducible colouring matters.
A part of the original solution is mixed with 20% KOH and warmed.</td></tr>
<tr><td>The liquid remains unchanged.
Colouring matters not reoxidisable.</td><td>The original colour restored.
Reoxidisable colouring matters.</td><td>Decolourisation or a precipitate.
Imino-carbo-quinone colouring matters.</td><td>No precipitation. The liquid becomes more coloured.
Oxy-carbo-quinone colouring matters.</td></tr>
<tr><td>Class I</td><td>Class II</td><td>Class III</td><td>Class IV</td></tr>
<tr><td>Nitro-, nitroso-, and azo colouring matters, including azoxy- and hydrazo-colours.</td><td>Indogenide- and imino-quinone colouring matters.</td><td>Amino-derivatives of di- and tri-phenylmethane, auramines, acridines, quinolines, and colour derivatives of thiobenzenyl.</td><td>Non-amino-diphenylmethane colouring matters, oxy-ketone colouring matters (most of the natural organic colouring matters).</td></tr>
</table>

[1] Some indulines are only decolourised with difficulty, the solution never becoming quite colourless.

TABLE B.

Group I.—Dyestuffs Reduced by Stannous Chloride and Hydrochloric Acid, the Colour not Returning on Oxidation.

Nitro-dyestuffs R.NO₂. Yellow or orange dyestuffs soluble in water, dyeing wool and silk directly, but not cotton. The aqueous solution tends to decolourise with hydrochloric acid. On partial reduction with hydrochloric acid and stannous chloride, they give red nitro-amino derivatives (nitramines) or nitrophenols turning red in KOH.	*Nitramines* soluble in ether in presence of KOH				$.N:R:N{<}^{O}_{OH}$	*e. g.*, Aurantia.
	Nitrophenols insoluble in ether in presence of KOH.	*Unsulphonated*, soluble in ether, in presence of acetic acid.			$O.R:N{<}^{O}_{H}$	*e. g.*, Victoria Yellow. Naphthol Yellow S.
		Sulphonated, in every case insoluble in ether.				
Nitroso-dyestuffs O:R:N.OH. Brown or green, usually insoluble in water. Dye indirectly. Give a blue colouration with sulphuric acid and phenol (Liebermann's reaction).	*Unsulphonated*, insoluble in alcohol, soluble in ether in presence of acetic acid.					*e. g.*, Dioxine.
	Sulphonated, soluble in water, insoluble in ether.					*e. g.*, Naphthol Green B.
Azo dyestuffs R.N:N.R. Recognisable as not belonging to either of the two foregoing subdivisions. Their aqueous solution treated with KOH and extracted with ether behaves as follows:	The solution is coloured, the colour being extracted by dilute acetic acid. *Basic dyestuffs.*	Unsulphonated amino-azo dyestuffs.			.R.N:N.NHR′	*e. g.*, Bismarck Brown.
	Coloured solution. The colour is not extracted by dilute acetic acid. *Neutral dyestuffs.*[1]	Hydroxyazo dyestuffs not containing a carboxyl group.			O.H.R.N:N.R′	*e. g.*, Soudan I.
	Colourless solution, acetic acid does not extract anything. *Acid dyestuffs.*	*Unsulphonated*, soluble in ether from dilute acetic acid.	Hydroxyazo dyestuffs with a carboxyl group.	Dye cotton indirectly.		Diamond Yellow.
				Dye cotton directly.		Chrysamin.
		Sulphonated, insoluble in ether from dilute acetic acid.	Non-amidated, unchanged by HNO[2].	Dye cotton indirectly.		Bordeaux B.
				Dye cotton directly.		Azo Blue.
			Amidated, react with HNO_2.	Dye cotton indirectly.		Fast Yellow N.
				Dye cotton directly.		Congo Red.

[1] Some amino-azo dyestuffs (Aniline Yellow) behave like neutral dyestuffs, but differ from these in being decolourised by nitrous acid.

[2] The presence of an amino group is detected by treating 5 c.c. of the warm solution with 2–3 drops of a 1% dilute acetic acid and the same quantity of a 1% potassium nitrite solution. Amino derivatives are decolourised or the colour is modified while non-amidated compounds remain unchanged or are not further affected than by acetic acid alone.

TABLE C.

Group II.—Dyestuffs Reduced by Stannous Chloride and Hydrochloric Acid, the Colour Returning on Oxidation.

The aqueous or alcoholic solution (5 c.c. of a strength 1:10,000), is treated with 4–5 drops of 20% KOH and extracted with 10–15 c.c. of ether. This solution washed with water (once with an equal volume if the original solution was aqueous, but 2–3 times if alcoholic), shows the following reactions:	The solution is *coloured* or *colourless*, but imparts the original colour to 5% acetic acid when shaken with it. *Basic Dyestuffs.*—Dye wool from an alkaline bath.	The solution is easily reduced by hydrochloric acid and stannous chloride in the cold.	*Oxazines* free from sulphur.	$N\langle^{R'}_{R=N\equiv}\rangle O$	*e. g.*, Nile Blue.
			Thiazines (contain sulphur).	$N\langle^{R'}_{R=N\equiv}\rangle S$	*e. g.*, Methylene Blue.
		The solution is only reduced with difficulty and frequently imperfectly. It requires to be warmed, with an excess of hydrochloric acid and stannous chloride.	*Indulines.*—Blue colour with concentrated sulphuric acid giving a blue solution on dilution with water.[1]	$N\langle^{R'}_{R=N\equiv}\rangle N$	Spirit-soluble Induline.
			Safranines. — Green colour with sulphuric acid turning blue and then violet on dilution.	$N\langle^{R}_{R}\rangle N:$	Safranine T. extra.
	Coloured.—The colour is not extracted by acetic acid. *Neutral Dyestuffs.*—Insoluble in water, soluble in alcohol; dye the fibre from an indigo vat.	Blue dyestuffs affected by warm hydrochloric acid.	*Indophenols*	$N\langle^{R}_{R=O}$	Indophenol.
		Red or blue dyestuffs unchanged by hydrochloric acid; give isatin with nitric acid.	*Indogenides*	$HN\langle^{R}_{C}\rangle CO$	Indigotin.
		Unsulphonated.—Soluble in ether in presence of acetic acid.	*Oxazones*	$N\langle^{R}_{R=O}\rangle O$	Fluorescent Blue, Orcein.
	Colourless, acetic acid does not extract anything. *Acid Dyestuff.*—Soluble in water, dyeing wool from an acid bath.	*Sulphonated.*—Not soluble in ether.	Easily reduced by stannous chloride and hydrochloric acid.	*Sulphonated Indogenides.*	Indigocarmine.
				Sulphonated Thiazines.	Thiocarmine R.
			Reduced with difficulty by stannous chloride and hydrochloric acid.	*Sulphonated Indulines.*	Water-soluble Nigrosine.

[1] The indulines and safranines differ in their basicity; the former can be liberated by ammonia and extracted by ether, while potassium hydroxide is necessary to obtain the safranine base.

TABLE D.

Group III.—Dyestuffs not Reduced by Stannous Chloride and Hydrochloric Acid having the Iminoquinone-carbon chromophore .N:R:C:

The aqueous or alcoholic solution of the dyestuff is treated with KOH, and then extracted with ether.	Coloured or colourless solution. The colour is extracted by 5% acetic acid. *Basic Dyestuffs.* Dye wool from an alkaline (NH_3) bath.	Colourless, non-fluorescent, ethereal solution. The solution in acetic acid is non-fluorescent. The aqueous solution is decolourised by potassium hydroxide and decomposed by hydrochloric acid.	*Auramines.*	$C\begin{array}{l}\diagup R\\ =N\\ \diagdown R\end{array}$	*e. g.*, Auramine O.
		Colourless, greenish, fluorescent, ethereal solution. The aqueous solution is precipitated by potassium hydroxide, and only slightly changed by hydrochloric acid. Nitric acid colours it red.	*Acridines.*	$-C\begin{array}{c}\diagup R\diagdown\\ \overline{\quad\quad}\\ \diagdown R\diagup\end{array}N$	Phosphine.
		Colourless or coloured non-fluorescent ethereal solution. The acetic acid extract is reddish-violet, blue, and green, without fluorescence. The aqueous solution is generally decolourised by potassium hydroxide on warming, and is turned yellow by hydrochloric acid (with the exception of the phenylated rosanilines).	*Rosanilines* (unsulphonated).	$C\begin{array}{l}\diagup R\\ -R\\ \diagdown\!\!\diagdown R=N-\end{array}$	Magenta.
		The ethereal solution is colourless, and does not fluoresce. The solution in acetic acid is pink and fluorescent. The aqueous solution is decolourized by potassium hydroxide.	*Pyronines* (direct cotton dyestuffs, are turned yellow by hydrochloric acid. *Rhodamines* (unsulphonated are unaffected by hydrochloric acid).	$-C\begin{array}{c}\diagup R\diagdown\\ \\ \diagdown R\diagup\end{array}O$	Pyronine G. Rhodamine S.
	The colour is not extracted by acetic acid from the coloured ethereal solution. *Neutral Dyestuffs.* Insoluble in water; soluble in alcohol.	The ethereal solution is yellow, and does not fluoresce. The alcoholic solution is yellow and non-fluorescent, and is unaltered by aqueous acids or alkalies.	*Quinophthalones*[1] (unsulphonated).	$-C\begin{array}{l}\diagup R\\ \\ \diagdown\!\!\diagdown R=N\equiv\end{array}$	Spirit soluble Quinoline Yellow.
	The ethereal solution is colourless; acetic acid does not extract anything. *Acid Dyestuffs.* All soluble in water, and dye wool from an acid (HCl) bath. The aqueous dyestuff solution is boiled with bleached cotton. The cotton is not dyed.	Yellow dyestuffs soluble in water, without fluorescence, unchanged by aqueous acids or alkalies.	*Sulphonated Quinophthalones.*		Water soluble Quinoline Yellow.
		Water soluble dyestuffs, reddish-violet, blue, or green, generally decolourised by potassium hydroxide solution, little affected by hydrochloric acid.	*Sulphonated Rosanilines.*		Magenta S.
		Red or violet dyestuffs giving fluorescent aqueous solutions not affected by potassium hydroxide, or only slightly.	*Sulphonated Rhodamines.*		Violamine R.
	The cotton is dyed.	Brownish-yellow or orange dyestuffs giving more or less fluorescent aqueous solutions, dyeing silk, wool, and cotton directly.	*Thiazoles.*[2]	$\begin{array}{l}-C=N\\ \;\;\mid\quad\;\mid\\ \;\;S-R\end{array}$	Primuline.

[1] The quinoline dyestuffs Berberine and Flavaniline have no definite chromophore, and are intermediate between the auramines and acridines.
[2] The thiazole dyestuffs are generally sulphonated with the exception of Thioflavine T, which, although soluble in ether, dyes wool from an alkaline bath.

TABLE E.

Group IV.—Dyestuffs not Reduced by Stannous Chloride and Hydrochloric Acid having the Oxyquinone-carbon chromophore O:R:C:

The alcoholic solution of the dyestuffs treated with a few drops of a dilute (1:1000) solution of ferric chloride.	Remains unchanged. *Non-aminated triphenylmethane dyestuffs*, generally soluble in water, dyeing wool directly.	The dyestuff is dissolved or suspended in boiling water.	It does not dye wool directly. Generally insoluble in water, soluble in alcohol without fluorescence.		*Aurins.*	$C{-}R' \quad \diagup R' \quad \diagdown\!\diagdown R{=}O$	Aurin.
			Dyes wool directly. Generally soluble in water and alcohol to fluorescent solutions.		*Phthaleins.*	$C{<}{R' \atop R'}{>}O \quad \diagdown\!\diagdown R{=}O$	Eosin.
	Turns green or olive-green. Oxyketone dyestuffs, generally insoluble in water, dye fibres indirectly.	The original dyestuff is treated with 1% KOH.	Dissolves with a yellow or reddish-yellow colour. *Monoketones.* — The alkaline solution is treated with an excess of hydrochloric acid.	Usually decolourised (with decomposition) especially on warming.	*Benzophenones.*	$CO{<}{R \atop R}$	Alizarin Yellow A.
				Gives an intense yellow without decomposition.	*Flavones.*	$CO{<}{R{-}O \atop C{:}C}$ (ring: CO–R–O–C:C)	Quercetin.
			Dissolves with a red, reddish-violet, blue, or green colour. *Diketones* (Quinones) — The alkaline solution is acidified with acetic acid.	The free acid is precipitated. Generally soluble in ether and dyeing the fibre indirectly.	*Anthraquinones* (unsulphonated).	$CO{<}{R \atop R'}{>}CO$	Alizarin.
				The dyestuff acid remains in solution, is insoluble in ether and dyes wool directly.	*Anthraquinones.* (sulphonated).		Alizarin Red S.

The following general methods of examination are of service in classifying the coal-tar colours:

1. Agitate a small quantity of the dye with dilute sulphuric acid and ether. On separating the ether and evaporating it to dryness, a residue will be left if the dye contain an unsulphonated acid dye, such as picric acid (or a picrate), a nitrocresolate (Victoria Yellow), a nitronaphtholate (Manchester Yellow), Aurin, an eosin, etc. The basic dyes are not removed from an acidified aqueous solution by agitation with ether, and hence a complete separation of the above-named substances may be effected by the careful employment of this method.

2. Another indication of the nature of a dye is obtained by adding dilute sodium hydroxide to the aqueous solution and warming. Basic coal-tar dyes, except those of the safranine class (safranine), are precipitated, while the solutions of acid dyes generally remain clear.

3. E. Weingärtner recommended for the distinction of soluble acid from basic dyes a reagent prepared by dissolving tannin in a dilute solution of sodium acetate. The preparation and application of this reagent are described on page 444.

4. By the action of titanous chloride solution in the presence of sodium hydrogen tartrate, triphenylmethane and diphenylmethane dyestuffs are converted into leuco-compounds, which are only reconverted into the corresponding dyestuffs by fairly strong oxidising agents, such as lead peroxide paste and acids, and not by mere atmospheric oxidation. By careful partial reduction with zinc dust and acetic acid azo dyes may be reduced to the corresponding hydrazo-compounds, which are reoxidised to the original dye by the action of the air, but it is by no means easy to stop the reduction at this stage; by energetic reduction with zinc dust and acetic or mineral acid or preferably by a titanous chloride solution containing free hydrochloric acid, azo-dyestuffs are converted into amino-compounds, the molecule being broken down. The resulting mixture of bases cannot be re-oxidised to the original dye, but an examination of the products of reduction may yield valuable information. Dyes of the indigo group, and also the indanthrene vat dyestuffs, are converted by alkaline reducing agents into solutions of leuco-compounds which are readily reoxidised by the air to the original dye. Sulphide dyes are decomposed by powerful acid reducing agents, such as titanous chloride and hydrochloric acid, with formation of hydrogen sulphide, but care must be taken to make sure that this does not arise from impurities in the

reagents, or from other compounds containing sulphur which may be present.

5. J. Spiller (*Chem. News*, 1880, **42**, 191) has shown that treatment of the sample with concentrated sulphuric acid affords a means of recognising coal-tar dyes, which are not charred by its action, under the following conditions: To apply the test it is merely necessary to heat a few grains of the solid dyestuff in a test-tube with concentrated sulphuric acid. Useful information can be gained by observing the absorption-spectrum of the coloured liquid produced. The property of yielding a colourless solution with concentrated sulphuric acid, the liquid becoming coloured on dilution, is a characteristic reaction of several *quinoline dyes*, and does not occur in the case of dyes of most other classes. Tabular statements of the indications of various dyes with concentrated sulphuric acid are given under each class of dyestuffs.

6. In the case of basic dyes, the determination of the nature of the acid may assist identification. Generally the basic dyes occur in commerce as hydrochlorides, but exceptions to this rule occur. To detect the acid-radical the solution of the dye should be precipitated with ammonia or soda, and the filtered liquid acidified with nitric acid and tested with silver nitrate. In some few cases, especially with safranine, the base of which is freely soluble in water, this method is not applicable, and it is necessary to add the silver nitrate to the acidified solution of the original dye. Double chlorides of the dye-base and zinc may be recognised by the presence of zinc in the ash left on incinerating the sample with ammonium nitrate, with the usual precautions to prevent the escape of zinc in the form of metallic vapour. Common salt is often present in dyes, and it is important not to mistake the chlorine existing in this form for that present as the hydrochloride of a basic dye. Sodium chloride will be left as a residue on igniting the dye. Or the substance may be dissolved in water, the dyestuff salted out with sodium sulphate, free from chloride, and the solution then tested in the usual manner with nitric acid and silver nitrate solution.

On ignition, the eosins leave residues, the solutions of which contain more or less haloid salts of the alkali-metals, and hence precipitate silver nitrate. But these dyes are not basic, and the colouring matter (containing one or more halogens in organic combination) can be separated from the common salt by agitating the acidified solution

of the dye with ether (compare page 474). The analyst must remember that many of the more recent dyestuffs, for example the halogenated indigos, contain halogens in organic combination.

The following list of those basic dyes liable to be met with in commerce in other forms than that of the hydrochloride may be of value:

Name of dye.	Formula of base	Form of combination.
Magenta; fuchsine; rosaniline; Aniline Red.	$C_{20}H_{20}N_3.OH$	Acetate.
Azaleine; fuchsine.	$C_{20}H_{20}N_3OH$	Nitrate.
Methyl-violet.	$C_{19}H_{13}(CH_3)_5N_3.OH$	Zinco-chloride.
Benzyl-violet.	$C_{19}H_{12}(CH_3)_5(C_7H_7)N_3.OH$	Zinco-chloride.
Methyl-green.	$C_{19}H_{12}(CH_3)_6N_3.OH + 2CH_3Cl$	Zinco-chloride.
Iodine green; Night Green.	$C_{20}H_{14}(CH_3)_6N_3.OH + 2CH_3Cl$	Zinco-chloride.
Benzaldehyde-green; Malachite-green.	$C_{19}H_{12}(CH_3)_4N_2.OH$	Oxalate; zinco-chloride; ferrico-chloride.
Phosphine.	$C_{19}H_{15}N_3$	Nitrate.
Nile Blue.	$C_{18}H_{18}N_3O$	Sulphate.
Methylene-Blue.	$C_{16}H_{18}N_3S.OH$	Zinco-chloride.

Nitrates, *acetates*, and *oxalates*, in a few cases in which they occur, can be sought for by the usual methods, in the filtrate from the precipitate produced on warming the dye with sodium hydroxide solution. *Picrates* may be sought for in the same, or the original solution may be strongly acidified with dilute sulphuric acid, and agitated with benzene or ether.

The great majority of commercial dyes are sold in the form of alkali or ammonium salts of sulphonic acids, as these are soluble in water, the principal exceptions being certain basic dyes, vat dyes, sulphide dyes, and dyes of the anthracene series.

The metals of the alkaline earths are very occasionally met with. Ammonium salts can be readily detected by the evolution of ammonia on warming the dye with sodium hydroxide solution. Other sulphonates on ignition will leave sulphites or sulphates, in which the metal can be readily identified. Of course, the presence of sulphates in the ash does not demonstrate the previous existence of a sulphonate, unless the absence of an added sulphate in the original dye has been proved. This may usually be effected by adding barium chloride to the highly dilute aqueous solution of the dye. In the event of a coloured precipitate being formed, probably consisting of the barium salt of the sulphonic acid, this should be filtered off, washed, and digested with a solution of ammonium carbonate, which will decompose, any

barium sulphonates forming barium carbonate, without affecting any barium sulphate present. On again filtering and treating the residue with dilute hydrochloric acid, any white insoluble residue must be tested for barium sulphate. Or more simply, the dye is salted out from aqueous solution with pure sodium chloride, filtered, and the colourless filtrate tested with barium chloride and hydrochloric acid.

The metallic radical of many acid dyes can be detected without igniting by precipitating a concentrated aqueous solution of the colouring matter with pure concentrated hydrochloric acid, which almost always precipitates the free acid. After filtration, the metal may be identified in the filtrate.

For the detection of the *halogens* existing in organic combination in the eosins and some other soluble dyes the substance should be dissolved or suspended in water, and the liquid acidified with dilute sulphuric acid and agitated with ether. The ethereal layer is then removed, evaporated, and the residue mixed with excess of calcium oxide, free from chlorides, and then heated to redness in a combustion-tube. The product is treated with water, dilute nitric acid added in quantity sufficient to effect solution and leave the liquid slightly acid, the liquid filtered, and a portion of the filtrate tested with silver nitrate. If any notable precipitate is produced, chlorides, bromides, and iodides are then sought for in the usual way. In the aqueous solution separated from the ethereal layer, metallic chlorides can be sought for directly by means of silver nitrate.

Halogens in organic combination in insoluble dyestuffs, such as halogenated indigos, may be tested for by ignition with quicklime as described above, after washing out any inorganic chlorides with water. Similarly halogens in azo dyes may usually be detected by precipitating the colour-acid with nitric or sulphuric acid from an aqueous solution, washing with water, or saturated sodium sulphate solution until free from chlorides and then igniting with excess of quicklime in the usual manner. It will often be found more convenient to filter and wash the free colour-acid on a piece of boiled out cotton fabric rather than on filter-paper, as in the latter case the filtration is often exceedingly slow.

Nitro-compounds, used as colouring matters, are of a yellow or orange-red colour. When warmed with metallic tin (or stannous chloride) and hydrochloric acid, they are converted into colourless amino-compounds, which do not become coloured again on exposure

to air. This behaviour distinguishes them, except Acid Naphthol-Yellow, from the eosin dyes, but not from azo-colours. The latter, however, are usually sulphonates, and are not removed from their acidified solutions by agitation with ether, as are the unsulphonated nitro-compounds, eosins, and most other phenolic dyes. The nitro-compounds also differ from the azo dyes by dissolving in sulphuric acid to form yellow or colourless solutions, whereas with the latter more brilliant and striking colours are produced. The solutions of nitro-compounds, or fibres dyed with them, are but slightly altered by hydrochloric acid (distinction from yellow azo dyes, which are reddened); while ammonia and sodium hydroxide tend to darken or redden the colour (distinction from Phosphine).

The various phthaleïns may be recognised by boiling the solution of dyestuff with potassium hydroxide and zinc dust, and examining the filtrate, after neutralisation with acetic acid, for bromine and iodine. Or the halogen may be determined by igniting the dyestuff with lime, dissolving in nitric acid and examining the solution.

Thiazines may be distinguished from oxazines by detecting the presence of sulphur by fusing the dye with potassium nitrate and sodium carbonate and testing the melt for sulphates.

If the dyestuff has been reduced by stannous chloride, the reduction product may be further examined after removing the tin with hydrogen sulphide. Azo dyestuffs on reduction give at least two primary amines, which can often be separated by means of ether. The reduced solution, after removing the tin with hydrogen sulphide, is treated with potassium hydroxide and shaken with ether. The non-sulphonated amines will dissolve in the ether, leaving the sulphonated amines in the aqueous layer. The latter may frequently be further identified by observing the characteristic azo-compounds formed with certain diazo-derivatives. The presence of a para-diamine is recognised by the thiazine reaction, which is a treatment of the solution freed from tin with ferric chloride and hydrochloric acid in the presence of hydrogen sulphide. In non-amino dyestuffs this reaction also affords a method of distinguishing between monazo and diazo dyestuffs, and is it also possible to decide whether a sulphonic acid group is in the side or middle ring, since in the former case a thiazine is formed, which in the presence of potassium hydroxide can be extracted with ether, whereas a sulphonated thiazine remains in the aqueous solution.

In examining small quantities of a dyestuff it may be convenient to examine the reduced solution microchemically for the various possible aminobenzenes and aminonaphthalenes (see Behrens, *Mikrochemische Analyse organischer Verbindungen*, Heft 3).

For the separation of mixed dyestuffs, Rota has suggested an extraction with ether. For instance, it is possible to separate basic from acid dyestuffs by adding a 20% solution of potassium hydroxide to the aqueous solution of the colouring matter and shaking with three times the volume of ether; the free bases will dissolve in the ether and leave the acid in the aqueous layer. The latter solution is neutralised with acetic acid and subsequently examined. The ethereal solution is washed with slightly alkaline water and then shaken with one-third of its volume of a 5% solution of acetic acid; the acid layer on evaporation leaves the dyestuff as a residue. Some dyestuffs are not extracted by the acetic acid, in which case they are obtained by evaporation of the ethereal solution.

The unsulphonated acid colouring matters may be separated by successive extractions with ether, by means of which they are separated into three groups:

(1) Those extracted by ether in the presence of 1% acetic acid solution.

(2) Those extracted by ether in the presence of hydrochloric or sulphuric acid.

(3) Those insoluble in ether.

By treating the ethereal solutions with water and dilute ammonia, a further separation can often be made (picric acid from Martius' yellow).

When a doubt exists as to the identity of a colouring matter, it is often of service to dye animal and vegetable fibres with it, and note its behaviour in an acid and alkaline bath, with and without mordants, and the colour reactions with these materials.

Examination of Commercial Colouring Matters.

In dealing with these substances it must be remembered that it is exceedingly difficult to obtain many of them in a chemically pure state. The practice of mixing inert matters with coal-tar dyes to bring the colours to a definite standard of strength, and sometimes with the additional object of direct adulteration, is very common. In some

cases, especially where the dyes are intended for exportation, the "standard" of strength is as low as 2.5% of actual colouring matter, and in other cases, if not carried so far, dilution is so generally practised that the pure colouring matters are almost unknown commercially (*Jour. Soc. Dyers*, 1888, **4**, 70).

Among the admixtures most largely used are common salt, sulphate of sodium, and dextrin. Sulphate of magnesium is also employed, as also oxalic acid and certain oxalates, sugar, dextrose, starch, etc. J. J. Hummel has described a sample of spurious magenta, consisting of crystals of potassium hydrogen oxalate, coated over with real magenta by steeping them in an alcoholic solution of the dye. Bronze-powder is said to have been employed for adulterating certain aniline dyes.

Water in paste-dyes (alizarins, etc.) may be determined by drying a known weight at 100° and observing the value, it must not be assumed that the weight of the residue represents the true colouring of the sample. The dry residue should be macerated with warm water in a mortar, and the solution filtered. The insoluble matter is then again weighed, or the dissolved matter is determined by evaporating an aliquot part of the solution, when a residue may be obtained, containing common salt, dextrin, dextrose, glycerin, etc.

The presence of *mineral matters* generally may be detected and determined by incinerating a known weight of the sample and weighing the ash, but it must be remembered that metallic oxides and alkali-metal salts are left on the ignition of many pure dyes. This will be the case with sulphonated dyes, double zinc salts, the salts of acid colouring matters, and many other dyes.

Common salt is so generally employed for salting out coal-tar dyes from their solutions, that its presence in moderate amount in non-crystalline colouring matters must not be mistaken for an intentional addition with a view to adulteration. An addition of silver nitrate to the solution must not be relied on for the detection of common salt unless the dye is one which does not contain the colouring matter in the form of a hydrochloride of the base, or yield an insoluble silver salt; but any chloride found in the ash left on igniting the sample probably existed as common salt, which usually can be recognised in the ash by this test. The eosins leave chlorides, bromides, or iodides on ignition; but if the aqueous solution of the colouring matter be acidified with dilute sulphuric acid and agitated with ether, the dye will pass into the ethereal layer, and after repeating the process until

extraction is complete, the aqueous layer may at once be tested for chlorides by adding silver nitrate.

The presence of *sodium sulphate* in the ash does not prove the existence of that salt as an adulterant of the original colouring matter, since sulphonated dyes usually leave a sulphate or sulphite of alkali-metal on ignition. The presence of a sulphate may be detected by the addition of barium chloride to the acidified solution of the original sample, but the precipitate obtained often consists wholly or largely of the barium salt of the sulphonated dye. On filtering, and treating the precipitate with ammonium carbonate, the sulphonate will be dissolved with formation of barium carbonate, and on then washing the residue and treating it with dilute hydrochloric acid any barium sulphate will be left undissolved and can be identified. Sodium sulphate is often present in the azo dyes, and may be detected by saturating the aqueous solution with chemically pure sodium chloride, when the sulphonated colouring matter will be precipitated, and the sulphate can be detected by adding barium chloride to the diluted and acidified filtrate. Sodium sulphate may frequently be detected, especially if present in any considerable amount, by carefully dissolving the dye-stuff in strong alcohol, when the sodium sulphate will be left as a white residue, which may be dissolved in water and tested with barium chloride.

The presence of magnesium in quantity in the solution or ash of a dye almost invariably indicates adulteration with *magnesium sulphate.*

Eosin dyes sometimes contain added *carbonates of alkali-metals*, which may be detected by the evolution of carbon dioxide on acidifying.

Dextrin is sometimes recognisable by its odour on dissolving the dye in warm water, or on heating it in a test-tube. Where it is desired to ascertain the amount, from 1 to 2 grm. of the colouring matter should be washed with strong alcohol, the residue dissolved in the smallest possible quantity of water, and the solution filtered into a tared beaker containing a weighed glass rod. Alcohol is then gradually added as long as a precipitate is formed, whereby the dextrin is separated in flocks, which on stirring become attached to the sides of the beaker. The liquid is poured off, and the beaker and glass rod rinsed with rectified spirit, dried at 100° or a slightly higher temperature, and weighed.

Sugar is sometimes employed as an adulterant of dyes. Crystallised magenta has been thus adulterated.

On spreading out such a sample on a piece of white paper placed in a strong light, the large fragments may be recognised by their edges being less deeply tinted than the genuine crystals of the dye. When removed and cautiously washed with strong alcohol, the sugar crystals become nearly colourless, and may be identified by the odour of caramel produced on heating. The amount of sugar when present may be ascertained in many cases with approximate accuracy by treating a known weight of the sample with absolute alcohol saturated with sugar, or with alcohol mixed with a little ether. A method of estimating sugar in magenta and other basic dyes consists in precipitating the hot aqueous solution by picric acid. The filtered liquid is treated with basic acetate of lead, again filtered, the lead in the filtrate removed by sulphuretted hydrogen or sulphurous acid, and the sugar estimated polarimetrically, or inverted and determined by Fehling's solution.

Starch is left insoluble on treating the sample with cold water or alcohol, and may be readily recognised in the residue by its microscopical characters and the blue colouration produced with iodine.

Arsenic is almost always present as an impurity in aniline dyes. It may be detected and estimated as described on page 249.

Antimony, copper and other poisonous metals are sometimes employed for mordanting dyes, and irritation of the skin and other ill effects have been attributed to their presence. The subject has been discussed at length by J. R. Ashwell and H. Forth (*Jour. Soc. Chem. Ind.*, **5**, 226, 301).

Foreign colouring matters may often be recognised by a judicious treatment with solvents, or more systematically as described in the preceding pages.

E. Knecht (*J. Soc. Dyers and Col.*, 1903, 169; 1904, 3, 9, 111, 292; 1907, 284) determines dyestuffs of very varying character quantitatively, both as such and on the cotton fibre, by reduction to colourless derivatives with a standardised solution of titanous chloride, $TiCl_3$, which is converted during the titration into $TiCl_4$. The titanous chloride solution is kept in an atmosphere of carbon dioxide, and the titrations are conducted in a continuous current of that gas. Soluble azo-dyestuffs, basic dyestuffs and eosins are titrated directly in presence or excess of sodium bitartrate at the boil, until the solution is colourless. Basic dyestuffs, methylene blue, safranines, etc., are reduced in this way to the corresponding leuco-compounds, while the azo dyestuffs are completely reduced, with formation of the corresponding

amino-compounds. The end-point is not sharp in the case of yellow dyestuffs and of nitro-compounds, if carried out as described above, and in these cases the compound is boiled with excess of the reagent until completely reduced, the liquid cooled, and titrated back with a standard solution of a ferric salt, in presence of potassium sulphocyanide until a permanent red colour is obtained. Insoluble nitro-compounds are either sulphonated or are dissolved in alcohol and the solution poured into excess of the reagent and boiled. The titanous chloride solution is standardised by titration with a ferric salt of known strength, which may be prepared by adding permanganate solution to a standard solution of ferrous ammonium sulphate containing free sulphuric acid until the latter is just pink. This is added until the titanium solution just gives a red colouration in presence of potassium sulphocyanide. A convenient titanous chloride solution is prepared by diluting 10 c.c. of commercial titanous chloride, together with 10 c.c. of concentrated hydrochloric acid, to 1 litre with water; this must of course be kept in an atmosphere of carbon dioxide. As an example of the method the following determination of pararosaniline hydrochloride may be cited: 1 grm. of the dyestuff was dissolved in water and made up to 500 c.c. 50 c.c. of this solution were taken, 25 c.c. of a 20% solution of Rochelle salt added, heated to the boil, and titrated with titanous chloride solution in a current of carbon dioxide until colourless. 17.35c.c. were required, of which 1 c.c. = 0.001622 grm. of iron. As the molecular weight of pararosaniline hydrochloride is 323, and this requires for reduction 2 atoms of hydrogen, equivalent to 112 parts of iron, the percentage of pure dyestuff is:

$$\frac{1000 \times 17.35 \times .001622 \times 323}{112} = 81.28\%.$$

Dyestuffs on dyed cotton fabrics are determined by Knecht by first boiling the weighed material with dilute hydrochloric acid, adding excess of standardised titanous chloride solution to the boiling liquid in a current of carbon dioxide, and titrating back the excess after cooling by means of standard iron solution, adding thiocyanate as an indicator. (See *New Reduction Methods* in *Volumetric Analysis* by Knecht and Hibbert, 1910; Longman, Green and Co.)

Another method of examining certain basic dyes consists in precipitating the solution by a standard solution of picric acid.

Night Blue employed for the purpose of ascertaining the value of certain colours. Rawson (*J. Soc. Dyer, and Col.*, 1888, **14**, 82) describes this method as applied to Naphthol Yellow. A standard solution of Night Blue is prepared by dissolving 10 grm. of the dyestuff in 50 c.c. of glacial acetic acid, and diluting to 1 litre with water. Solutions of samples of Naphthol Yellow S are prepared containing 1 grm. per litre. 10 c.c. of the solution of Night Blue are placed in a small flask and the solution of Naphthol Yellow is run in from a burette until a portion of the liquid on filtration shows a yellow tint. The value of the samples examined will be in inverse proportion to the number of c.c. required to precipitate 10 c.c. of Night Blue solution. The latter may be standardised by the use of pure crystallised Naphthol Yellow S, and the percentage of pure dyestuff in the sample may thus be found. 1 gram. of commercial Night Blue will precipitate about 0.25 grm. of pure dry Naphthol Yellow S; it would thus appear that 2 molecules of Night Blue combine with or precipitate 1 molecule of Naphthol Yellow S.

This method is said to be applicable in general to the valuation of azo dyes; but care should be observed that in the comparison of two dyestuffs they should possess a similar constitution. But samples of the same dyestuff can be compared by this process with fair success.

A simple and useful means of examining colouring matters is by making a solution and diluting it with water or alcohol (as the case may require) until the depth of colour is identical with that of a solution of known concentration made from a standard specimen. The operation is conducted in a manner similar to the Nessler test for ammonia in water, or the colorimetric determination of carbon in steel.

The following process of estimating adjective and some other colours is given by W. P. Dreaper (*J. Soc. Chem. Ind.*, 1893, **12**, 977). The dye (paste or powder) is titrated at 95° with a standard solution of copper sulphate (30 grm. per litre) in the following way: 1 grm. of paste or 0.25 grm. of powder is transferred to a flask, 10 c.c. of a solution containing 100 grm. of sodium acetate and 5. c.c. acetic acid to 1000 c.c., added and the volume made up to 50 c.c. with water. 1 grm. of barium sulphate is introduced and the copper solution run in with constant stirring. Toward the end of the titration the solution may be brought up to the boil for a minute or so.

In the case of Alizarin S and SSS (powder) which are sodium salts

of sulphonic acids of alizarin, no precipitate is formed. In this and similar cases barium chloride must be added to the solution before titration to form the barium salt. The action then proceeds regularly. The bisulphite compounds such as Alizarin Blue S. R. W. (powder) are precipitated by copper sulphate.

Diamine Fast Red F. gave constant results in the presence of $BaCl_2$, showing that dyes containing one carboxyl and a hydroxyl group in the ortho position, and also a sulphonic acid group, may be titrated in this way. The following results may be given as examples.

Dye	CuO pptd. per grm. of dye
Alizarin bordeaux B 20%	.0527
Gallein paste	.0489
Cœrulein S. powder	.1931
Alizarin Red GI 20%	.0436

The end-point is obtained by filtering a drop of the solution through a small double square of Swedish filter-paper and testing the under fold, which is free from any precipitate or lake, with a drop of potassium ferrocyanide solution which will produce the usual pink colouration in the presence of any excess of copper in the solution.

It will be often found in practice that evidence as to the general nature of any dye may be of value apart from its actual identification, which may be a matter of extreme difficulty in some cases. The information as to whether it be a direct dye (that is one which will dye on cotton without a mordant), or whether it is a mordanted, "developed," or vat dye as instanced by its fastness against milling, or boiling in soap or alkaline solution may be the determining factor in its commercial use. These points must be remembered and for such reasons as these, and others, the almost universal method of assaying aniline dyes, both for purity of tone and amount of colouring matter, is to compare the dyeing power of the sample with that of a sample of known purity. 1 to 5 grm. of each specimen is dissolved in 1,000 c.c. of water and dyeing operations which vary with the different fibres, or class of dyes, are conducted under identical conditions so far as concentration of solution, temperature of dyeing, and such factors are concerned. In the case of wool equal weights of bleached and scoured wool may be dyed in each

solution. The condition of dyeing as regards the addition of assistants, acids, etc., should follow the general methods of dyeing. In the case of adjective dyes where mordants are required the skeins or swatches must be previously'mordanted. In the case of ingrain, vat, or sulphide dyes the necessary conditions governing the dyeing action must also be complied with. It is very difficult to indicate any general method of procedure, but in the case of wool where the dye-baths are heated in a common bath by steam or water, the temperature of the dye solution may gradually be brought up to 95° and kept there for 1 hour. Cotton may be dyed up to 100°, and silk in the ordinary way up to 80°. Raw or gum silk is not dyed above 60°.

Where cotton, silk, artificial silk, ramie, or other fibres are concerned. it may be necessary to test the dye under the special conditions necessary for the dyeing of these respective fibres. In the case of a new adjective dye it is advisable to test its value on several mordants, even on those less commonly used, like nickel or cobalt. For the necessary conditions for these extended tests the standard books on dyeing may be consulted.

Many dyes cannot be completely withdrawn from their solutions, and in such cases the method is not so readily applicable. In some instances, mixtures of dyes can be detected by dyeing in sequence small portions of wool in the same dye bath, when the colour fixed will often be notably different in tint, owing to the varying affinity of different dyes for the fibre.

Special methods of applying laboratory dye-tests to certain colouring matters are described in the preceding sections.

III. Physical Examination of Dyed Fibres.

W. Stein (*Dingl. polyt. Jour.*, **210**, 245) gave the following directions for testing the *fastness of dyes* on coloured fibres. They must be received with reservation so far as the newer coal-tar dyes are concerned: *Red* dyes should not colour lime-water or soap solution when dyed therewith, and the fabrics themselves should not be altered in colour by this treatment. A negative result when thus treated indicates the absence of brazil-wood, archil, safflower, sandal-wood, and many coal-tar dyes. *Violet* dyes may be regarded with suspicion if they yield any considerable quantity of their colour when boiled with a mixture of equal parts of rectified spirit and water and left to stand for fifteen minutes; or if, on boiling with dilute hydrochloric acid, they change

in colour to brown or brownish-red, and colour the liquid red. Fast *blue* dyes should not give up any colouring matter when boiled with alcohol or warmed with a mixture of hydrochloric acid with water and alcohol. *Green* dyes when boiled with alcohol should not colour the liquid either blue, green, or yellow; and hot hydrochloric acid should not acquire a red or a blue colour from green fabrics. *Orange* dyes should not be dissolved from the fibre by boiling water or warm alcohol. *Brown* dyes may not be considered fast if they colour boiling water red, or give a yellow colour to alcohol when left in contact with it. If a *black* fibre, when boiled with dilute hydrochloric acid, colours the liquid merely yellow, it may be considered fast, as, for instance, tannin-black; and if the colour of a fresh portion is changed to brown when boiled with a solution of sodium carbonate, there is probably only tannin-black present. If the fibre thus treated remains black or turns blue, it is probably bottomed with indigo under the tannin-black; while if the fabric colours hot dilute hydrochloric acid red, and is itself turned brown by the treatment, it is dyed with logwood-black, and may be considered unstable; but if when boiled with acid the fabric becomes blue and colours the liquid red, it is logwood-black bottomed with indigo.

The power of a dyed colour to withstand the action of certain tests either chemical or physical is of considerable importance in determining the suitability of a dyestuff for a particular purpose. The *fastness* of colours has reference to their permanence against the action of *light*, *washing*, *fulling*, *acids*, *alkalies*, *stoving* (sulphur), *bleaching* (chlorine), *ironing* (calendering), *rubbing* and *perspiration*. The required degree of fastness of any colour will, of course, depend on the use to which the dyed material is to be put, some goods requiring very fast dyes, whereas others do not. In order to determine the fastness of any dyestuff to the various agencies above enumerated, it is necessary to make experimental tests on a piece of fabric dyed with the colouring matter in question.

Light Test.—A sample is exposed to the action of direct light for 10 days; it is best to arrange the sample in such a way that one half is exposed while the other half is shielded. The exposure should be made in diffused north sunlight. Comparative tests are made with standard dyeings.

Washing Test.—This is carried out by scouring a small sample of the dyed material in a bath containing 10 to 15 grm. of neutral

soap per litre at a temperature of 49 to 60°. The sample should be immersed in the solution for 15 minutes, then washed and dried. If the colour is abstracted from the fibre in any appreciable degree it cannot be considered fast to washing or scouring.

Fulling Test.—A sample of the material is twisted together with white wool and cotton, and steeped in a soap bath similar to the above, only a small amount of soda ash (5 grm. per litre) is added. The sample should be squeezed and twisted with the fingers in order to simulate the action of fulling. If the colour bleeds into the white, the dye is not fast.

Acid Test.—For woollen materials a sample should be soaked in a 10% solution of sulphuric acid at 60°, after which it is washed and dried. For cotton fibres acetic acid at 38° should be used. The acid test also represents fastness to perspiration.

Alkali Test.—A sample of the dyed material should be steeped for 10 min. in a solution containing 10 grm. of soda ash per litre at 50° to 60°, washed and dried. This test is sometimes performed by sprinkling the material with milk of lime, allowing it to dry in and then brushing off. Fastness to alkali represents resistance to action of street dust, alkaline country air, etc.

Stoving Test.—A sample of the dyed material is subjected to the action of sulphurous acid fumes or solution for several hours.

Bleach Test.—A sample of the dyed material is steeped for 10 min. in a solution of bleaching powder at 0.5° Tw.

Ironing Test.—A sample of the dyed fabric should be slightly moistened, placed between 2 pieces of muslin, and pressed with a hot iron.

Hydrogen Peroxide Test.—Steep a sample of the dyed fabric for 1 hour in a cold solution of hydrogen peroxide (10 vols.). This is said to represent the fastness of a dye to out-door atmospheric exposure.

Water Test.—This is applied exclusively to silk; a sample of the dyed material is twisted with white silk and steeped for 12 hours in cold distilled water.

Rubbing Test.—A piece of the dyed fabric should be vigorously rubbed on a white surface of paper or cloth.

The actual loss in colour observed under the action of light is difficult to estimate in exact terms. Lovibond uses his tintometer for the purpose, and some of the results obtained are shown in the curves on page 440. Gebhardt (*J. Soc. Dyers and Col.*, 1910, **26**, 173) proposes

to register the general colour change in terms of grey by photographing the shades on orthochromatic plates through a filter corresponding to the original shade. Under these conditions the true loss in colour is said to be registered, only the rays reflected from any unchanged particles of the colour registering themselves upon the plate. Whether these conditions are those actually required is perhaps open to question. Working under standard conditions of exposure to artificial light, and with 6–10 standard shades of grey for general comparison, the results obtained may be indicated by the following examples:

Dyestuff	Fibre	Method of dyeing	Exposure to light	Degree of fading
Dianil Blue...	Mercerised cotton.	50% NaCl. 1% colour. 1½ hrs. boil.	100 hrs.	5.
Indigo........	Wool.	2% colour	100 hrs.	1.

Lovibond used a northern light; Gebhardt, an artificial one.

Moisture plays a very important part in such trials and its effect must in some way be allowed for in exact work of the nature indicated. The influence of acid, alkalies, and also effect the result, so that the actual conditions suggested for dyeing by the makers should be closely followed. As a general rule, the rough and ready method of exposing to a northern light and estimating the loss of colour by the eye is adopted in practical dyeing.

See also Heermann's *Koloristiche und Textil-chemische Untersuchungen*, Berlin, 1903.

IV. Chemical Examination of Dyed Fibres.

The recognition of artificial colouring matters on fibres is comparatively simple when only one dye is present, especially if no mordant has been employed. But when two or more dyes have been used, either in conjunction or succession, as is very frequently the case, the problem becomes very complicated, and the difficulty is further increased when the natural colouring matters and the mordants generally accompanying their use have also to be taken into account.

In many cases, the identification of a dye is greatly facilitated by a knowledge of the mordant present. Where the mordant is inorganic, its nature is best ascertained by examining the ash left on igniting the

fibre.[1] Organic mordants, such as tannin and albumin, are difficult to recognise in presence of colouring matters, and must be sought for by their special reactions. Fibres dyed with azo dyestuffs usually leave but little ash on ignition, as they require no mordant on silk or wool, and on cotton are usually fixed by means of tannin. On the other hand, alizarin dyes leave an ash containing a notable quantity of alumina or oxides of iron or copper; while the ash of fibres dyed with cochineal, brazil-wood, etc., will be found to contain either alumina or oxide of tin. Logwood-black and the wool dyestuffs are mordanted with chromium and occasionally copper, while iron is a constituent of some blacks and violets, as also of prussian-blue, as present in tannin blacks on silks. Lead is found in chrome-yellow, and is the base of vermilionette. Nickel, vanadium and copper are now employed for mordanting certain dyes, and antimony is also used.

The behaviour of the principal colouring matters on the fibre has been to a great extent described in the special paragraphs relating to the different dyes. Detailed and tabulated methods of examining dyed fabrics have been published by Fol (*J. Chem. Soc.*, **28**, 193), Stein (*Zeits. Anal. Chem.*, 1840, **9**, 520), Joffre (*Farb. Must. Zeit.*, 1882, 301, 496), and other writers. R. Martinon (*J. Soc. D. and Col.*, 1887, **3**, 124) has published a scheme for the detection of dyes on *silk*, and G. Dommerque (*Monit. Scient.*, 1889, **33**, 25) a similar method for the recognition of dyes on wool. A more general tabulation of reactions has been published by J. J. Hummel (*Dyeing of Textile Fabrics*), and this has been supplemented by R. Lepetit (*J. Soc. D. and Col.*, 1888, **4**, 133).

Knecht and Rawson, and Lehne, Rusterholz and Millikin have also published very comprehensive tables.

Examination of Red-dyed Fibres.—The red dyes are very numerous and often difficult to identify, and hence the following hints may possibly be found useful in special cases.

1. Boiling *alcohol* removes magenta, Safranine, Corallin, Aurin,

[1] Inorganic mordants may be tested for in the following manner:

Chromium:—Ash yellowish-or brownish-green; on fusion with potassium chlorate and sodium carbonate a yellow mass is obtained, which if dissolved in water and acetic acid gives a yellow precipitate with lead acetate.

Iron:—Ash is reddish-brown in colour; dissolved in hydrochloric acid it gives a blue precipitate with potassium ferrocyanide.

Copper:—Dissolve the ash in hydrochloric acid, add slight excess of ammonia, and filter; a blue filtrate indicates copper; after acidifying with acetic acid potassium ferrocyanide gives a reddish-brown precipitate.

Aluminium:—Ash is white; dissolved in hydrochloric acid, the addition of ammonia gives a white precipitate.

Tin:—Ash is white; may be reduced to metallic globules by heating on charcoal.

Titanium, *Nickel*, etc., by their ordinary reactions.

Spirit, Eosins, Orchil, Sandal- and Bar-wood, but does not greatly affect tissues dyed with red and claret azo dyes, Acid Magenta, Magdala-Red, alizarin and madder-dyes, cochineal, safflower, brazil-wood, lac-dye, or kermes, and does not extract soluble eosins if well dyed. Purpurin is partially extracted, colouring the alcohol red. Magenta, Safranine, and Orchil also colour the alcohol red, and santal-wood yellowish-red, but the others form yellowish, brownish, or nearly colourless solutions. On evaporating the alcoholic solution to dryness, and treating the residue with strong sulphuric acid, magenta yields a yellow or brown solution, but Safranine produces a fine green colour, changing through various tints by gradual addition of water.

2. Magenta may be distinguished from Orchil-red and Aurin by treating the fibre with *amylic alcohol*. This is coloured bluish-red by magenta, pink or violet by Orchil, and yellow by Aurin. On shaking the coloured amylic alcohol with ammonia, it is decolourised if the dye be magenta, but the colour will be unchanged if Orchil, and turned bluish-red if Aurin be the colouring matter present.

3. *Ether* removes Corallin, Aurin, and eosin more or less perfectly. Tissues dyed with Turkey-red acquire a dull cherry-red colour, and the ether leaves a brilliant scarlet residue on evaporation. This, when boiled with sodium hydroxide, yields a purplish-blue solution, from which acids precipitate orange-coloured flakes of alizarin.

4. By boiling with *ammonia*, Corallin, Aurin, and the eosins are usually dissolved from the tissue, the liquid being coloured pink or red.[1] On removing the tissue and agitating the liquid with ether and an acid, the colouring matters are extracted from the aqueous liquid, and may be detected in the ethereal solution by separating it, and evaporating to dryness or agitating with ammonia. Safflower colours ammonia salmon-tint. On the azo-reds ammonia usually has no action, and the same remark applies to alizarin and magdala red. Fibres dyed by magenta and Acid Magenta are decolourised, and Safranine gives a pink solution. The vegetable colouring matters usually behave as with sodium hydroxide.

5. On moistening the fibre with a dilute solution of sodium hydroxide (5 to 10%), the colour due to rosaniline is very gradually destroyed.

[1] When boiled with concentrated solution of sodium hydroxide (20–40%), Eosin G gives an orange-red solution, which on continued boiling becomes purple, and finally blue, with a strong green fluorescence. Neither the colour nor the fluorescence is changed by dilution. Eosin B, when similarly treated, gives a bluish-violet solution, with pale green fluorescence. On dilution, the liquid becomes reddish-purple. Eosin BN, when boiled with potassium hydroxide, gives eventually an olive-green non-fluorescent solution.

Safranine remains unchanged, but safflower is turned pale yellow, the original tint being restored by an acid. Cochineal gives a purple solution. Aurin, Corallin, and eosin behave as with ammonia. From fibres dyed with brazil-wood sodium hydroxide extracts much of the dye, cotton being almost decolourised, and the solution becoming bluish-red. Bar-wood and santal-wood give no colour to the liquid, but the fibre becomes purplish. With orchil the fibre becomes bluish-purple, and with Magdala-Red a dirty violet.

6. On treating the tissue with moderately strong *hydrochloric acid* (sp. gr. 1.11), magenta is turned brown or yellow, but the colour is restored by washing with water. Hydrochloric acid does not change the colour of fibres dyed with Acid Magenta, but the liquid acquires a faint bluish-red colour. Safranine is unchanged by dilute acid, but with strong acid a blue colour is produced, restored to red by washing with water. Turkey-red is unchanged. The azo-reds are usually (but not invariably) turned more or less violet, a coloured liquid being extracted. Of the azo dyes from benzidine, etc., fibres dyed with Congo-Red are turned blue-black by hydrochloric acid, and Delta-purpurin, Benzo-purpurin 2 B, and Congo-Corinth give similar reactions. With Rhodamine the fibre is turned a dirty brick-red without the liquid being coloured. The original hue is restored by washing. The eosins are turned yellow or brownish-yellow. Tissues dyed with brazil-wood are turned bright orange by dilute acid, and those dyed Corallin, Aurin and cochineal yellow. Ammoniacal cochineal, however, is unchanged by dilute acid.

7. On boiling the tissue in an aqueous solution of aluminium sulphate the liquid will become reddish with many dyes, and in the case of madder-red or purpurin will show a green fluorescence. On adding an equal measure of acid sodium sulphite to the red liquid, the solution will be bleached if the dye be Magenta, Safranine, Corallin, safflower, brazil-wood, or santal-wood, but not bleached if the colour be due to Orchil, cochineal, lac-dye, or kermes.

8. On igniting the fibre, the red coal-tar dyes usually leave very little ash, as they require no mordant on silk and wool, and on cotton are usually fixed by means of tannin. On the other hand, madder-red and pink leave an ash containing a notable quantity of alumina, and the ash of tissues dyed with cochineal or brazil-wood, or other dye-woods, will usually be found to contain either alumina or oxide of tin.

E. Knecht (*J. Soc. D. and C.*, 1905, 296) tests fibres for Paranitrani-

line Red by holding a very small flame at a distance of about 3/4 in. below the fabric for a few seconds. Paranitraniline Red is volatilised under these conditions and deposits on a piece of white paper (or calico) laid on the cloth. Naphthylamine Red behaves similarly, and so does indigo, but in this latter case the deposit is of course blue. It is sometimes possible to obtain confirmation of the dyes used on textile fibres by examining the samples by light from different sources; even if chemical tests indicate that two samples of material are dyed with the same dye, or dyes, and they give different shades (by comparison) in gas light as compared with daylight, it may be assumed that the dyes are not the same in both cases.[1]

Identification of Dyestuffs on Animal Fibres.—A scheme for the identification of dyestuffs on animal fibres, more especially on wool, has been worked out by A. G. Green, H. Yeoman and J. R. Jones (*J. Soc. D. and C.*, 1905, 9, 236) and is given below. It depends in the first case on methods for ascertaining the dying properties of the dye-stuff, and then its behaviour when reduced by sodium hydrosulphite and reoxidised, either by the air or by sodium persulphate.

The following is the general behaviour of various chemical groups of dyestuffs upon animal fibres towards reduction and subsequent oxidation:

Decolourised by sodium hydrosulphite.				Not decolourised, but changed to brown. Original colour restored by air or persulphate.
Colour restored on exposure to air.	Colour not restored by air, but on oxidation with persulphate.	Colour not restored either by air or persulphate.	Not altered by hydrosulphite.	
Azines, Oxazines, Thiazines, Indigo.	Triphenyl-methane group.	Nitro-, Nitroso-, and Azo-groups.	Pyrone, Acridine, Quinoline, and Thiazole groups. Some members of Anthracene group.	Most dyestuffs of the Anthracene group.

Having ascertained both the dyeing group and the chemical relationship of the colouring matter, and taking the shade also into consideration, the question when only one dye is present is usually narrowed

[1] Great difficulty is often experienced in practice though shades matching in daylight being quite different in artificial light.

down to a single representative or to a choice between a very few closely related dyestuffs. For distinguishing between these the behaviour with concentrated sulphuric acid or strong hydrochloric acid can be frequently employed. In the appended tables the sub-division of the groups has been usually omitted as unnecessary but is given in a few instances (see Table II) in order to illustrate the general method. For additional confirmation it is necessary to compare the sample both as to shade and reactions with a dyed pattern of the dyestuff to which it is believed to correspond.

In a scheme of this description some variation will be found in the sharpness of the indications with individual dyestuffs. Practice and experience is required before certainty can be obtained.

In the appended tables all groups of dyestuffs were considered, although in individual instances many of them would be at once excluded on account of the nature of the material or its shade. In such cases, therefore, the analytical scheme may be simplified.

Reagents.

The following reagents are employed. It is important that they should be of the strength indicated:

Dilute ammonia (1 : 100). 1 c.c. conc. ammonia. 100 c.c. water (soft or distilled).

Aqueous alcoholic ammonia. 1 c.c. conc. ammonia. 50 c.c. strong alcohol or methylated spirit. 50 c.c. water.

Dilute acetic acid (5%). 5 c.c. glacial acetic acid. 95 c.c. water.

Dilute alcohol (1 : 1). 50 c.c. strong alcohol or methylated spirit. 50 c.c. water.

Dilute hydrochloric acid (1 : 10) 10 c.c. conc. hydrochloric acid. 100 c.c. water.

Sodium hydroxide (10%). 10 grm. solid sodium hydroxide in 100 c.c. of solution.

Hydrosulphite A.—A 10% solution of hydrosulphite NF (Meister) or hydraldite (Cassella), *i. e.*, the formaldehyde compound of sodium hydrosulphite. This solution, which is slightly alkaline, is employed in most cases. In a few other cases, however, in which the reduction is more sluggish (*e. g.*, azo-yellows), it has been found necessary to employ a slightly acid solution. This is termed

Hydrosulphite B.—Prepared by acidifying 200 c.c. of hydrosulphite A with 1 c.c. of glacial acetic acid.

Persulphate.—A cold saturated solution of potassium persulphate.

Sodium Acetate (5%). 5 grm. crystallised sodium acetate. 100 c.c. water.

Procedure.—The tests are performed in test-tubes with pieces of the material about 3/4 inch to 1 inch square, which are covered with about 1 inch to 1.5 inch of the reagent. The tests should be carried out exactly as described. In making "stripping tests" the degree of stripping is judged by comparing the depth of shade remaining with that of the original pattern. The colour of the stripping solution is misleading, and can scarcely be relied upon as a guide. It is found advantageous in boiling with dilute acetic acid and dilute ammonia to repeat the extraction, as a better stripping is thereby obtained, and also with acid dyestuffs any staining of the cotton by the first strong extract is avoided. In testing with dilute ammonia or sodium acetate, the piece is placed in a test-tube with a somewhat smaller piece of white mercerised cotton cloth, and boiled for the time prescribed. With pale shades the size of the sample should be increased and that of the cotton diminished. The dilute ammonia is replaced by aqueous alcoholic ammonia in the case of the violet and black dyestuffs (Tables III and VII), as in these cases the acid dyestuffs are less easily extracted and the cotton is more liable to be stained by them. In making reduction tests, the sample is boiled for from 1/4 to 1 minute with the hydrosulphite, then rinsed well under the tap, and allowed to lie on white paper for an hour or so. With most dyestuffs which form air-oxidisable leuco-compounds, the colour returns immediately or in a few minutes, but with others a longer time is required. The reaction is accelerated by exposing the pattern to ammonia vapour. If the colour does not return the pattern is boiled in a test-tube with water, and potassium persulphate is added drop by drop, carefully avoiding an excess. If this also fails to cause any return of colour, the dyestuff is to be regarded as an azo-compound. The depth of the restored colour varies greatly in different cases; while with some dyestuffs the colour reappears with nearly its original depth, with others (probably on account of the greater solubility of their leuco-compounds) only a light shade may return. Safranine and its azo derivatives yield on reoxidation of the leuco-compound a violet colour. This is due to the condensation of the leuco-safranine with the formaldehyde present in the hydrosulphite NF.

The reactions given in the annexed analytical tables were mostly

ascertained upon wool fibre, but from a number of tests which were also conducted for a comparison upon silk, there is no reason to believe that the latter fibre will exhibit any variations in behaviour.

Examination of Yellow or Orange Shades.

(See Table I.)

The fibre may be dyed with one of the following colouring matters:

1. A basic acridine dyestuff, such as Phosphine, Benzoflavine, Rheonine, Acridine Yellow, Acridine Orange, Patent Phosphine, etc.
2. Auramine O and G.
3. Thioflavine T.
4. A basic azo dyestuff, *e.g.*, Chrysoïdine, Tannin Orange, New Phosphine, or Janus Yellow.
5. Quinoline Yellow, Uranine, Eosin Orange.
6. Tartrazin, Orange G, 2G, R, etc.
7. Naphthol Yellow S, Martius Yellow (nitro group).
8. Fast Yellow, Indian Yellow, Azoflavine, Curcumein extra, Orange II., Metanil Orange.
9. Metanil Yellow, Orange IV.
10. Thioflavine S, Chromine, Primuline, Chloramine Yellow, Chloro-phenine, Diamine Fast Yellow B or FF, Thiazole Yellow, Clayton Yellow, etc. (thiazole group). Also turmeric.
11. Curcumin S, Direct Yellows, Stilbene Yellows, Naphthamine Yellows, Mikado Yellows, Diphenyl Citronin, Mikado Oranges, etc. (stilbene group).
12. Chrysophenin Yellow, Chrysamin, Carbazol Yellow, Cresotin Yellow, Diamine Yellows, Benzo Orange, Congo Orange, Diamine Orange, Pluto Orange, Dianil Orange, Toluylene Yellow and Orange, Pyramine Orange, etc. (azo group).
13. Fustic, quercitron, or weld (on Al or Cr), alizarin Yellow A, Galloflavine, etc.
14. Alizarin Orange.
15. A mordant azo dyestuff, such as Alizarin Yellow G and R, Anthracene Yellow C, Flavazol, Diamond Flavine, Metachrome Yellow, Metachrome Orange, Chrome Orange, etc.

Examination of Red Shades.

(See Table II.)

The fibre may be dyed with one of the following colouring matters:

1. A basic red or pink of the pyrone group, such as Rhodamines, Irisamine, Anisoline, Pyronines, Rhodines, etc.

2. A basic red of the azine group, such as Safranine, Induline Scarlet, Rhoduline Red, Rhoduline Pink, etc.

3. A basic red of the triphenylmethane group, *e.g.*, Magenta, Isorubine, Fuchsine, Cerise, etc.

4. A basic azo dyestuff, *e.g.*, Janus Red.

5. A soluble red wood, such as brazil-wood, Lima wood, peach wood, etc.

6. A phenolic dyestuff of the pyrone group, *e.g.*, Eosin, Phloxin, Erythrosin, Safrosin, Rose Bengal, etc.

7. An acid dyestuff of the pyrone group, such as Fast Acid Eosin, Fast Acid Phloxine, Acid Rhodamine, Acid Rosamine, etc.

8. An acid azine, *e.g.*, Azocarmine, or Rosindulines.

9. Acid magenta (triphenylmethane group).

10. An acid azo scarlet or azo red, such as Xylidine Scarlet, Palatine Scarlet, Fast Reds, Bordeaux, Cloth Reds, Azofuchsine, Lanafuchsine, Sorbin Red, Chromotropes (unchromed), etc.

11. Cochineal Scarlet (tin mordant).

12. Orchil (cudbear).

13. A salt dyestuff, such as Diamine Scarlet, Diamine Red, Benzopurpurin, Hessian Purple, Rosophenine, Erica, Geranines, Anthracene Red, Bordeaux extra, etc.

14. Cochineal crimson (Al mordant).

15. Alizarin Reds or Acid Alizarin Reds.

16. An insoluble red wood, such as camwood or barwood.

17. A mordant azo colour.

Examination of Violet or Purple Shades.

(See Table III.)

The fibre may be dyed with one of the following:

1. A basic violet of the azine, oxazine, or thiazine groups, such as Neutral Violet, Rhoduline Violet, Rosolane, Iris Violet, Tannin Heliotrope, Methylene Violet, etc.

2. A basic violet of the triphenylmethane group, such as Methyl Violet, Crystal Violet, Benzyl Violet, Regina Purple, etc.

3. An acid violet of the pyrone group, *i.e.*, Fast Acid Violets or Violamines.

4. An acid violet of the triphenylmethane group, *i.e.*, Acid Violets, Formyl Violets, etc.

5. An alkali violet of the triphenylmethane group.

6. A red shade soluble blue (triphenylmethane group.)

7. An acid colour of the azine, oxazine, or thiazine groups, such as Induline or Fast Blue R.

8. An acid azo colour, such as Lanacyl Violet, Victoria Violet, etc.

9. A salt dyestuff, such as Hessian Violet, Diamine Violet, Oxamine Violet, Benzo Fast Violet, Columbia Violet, Oxydiamine Violet, Chlorantine Violet, etc.

10. Galleïn.

11. Alizarin on iron or chromium mordant.

12. Alizarin bordeaux.

13. Mordant dyestuffs of the oxazine group, such as Gallocyanine, Prune, Celestine Blue, etc.

14. Chrome Violet (mordant dyestuff of triphenylmethane group).

15. Mordant azo colours.

Examination of Blue Shades.

(See Table IV.)

The fibre may be dyed by one of the following colouring matters:

1. Basic dyestuff of the azine, oxazine, or thiazine group, such as Methylene Blue, Nile Blue, Capri Blue, Cresyl Blue, Meldola's Blue, etc.

2. A basic safranine-azo colour, *e.g.*, Indoine or Janus Blue.

3. A basic dyestuff of the triphenylmethane group, such as Victoria Blue, Night Blue, Brilliant Milling Blue B, etc.

4. Logwood Blue.

5. Indigo extract or indigo carmine (indigo sulphonic acids).

6. Thiocarmine (thiazine group).

7. Prussian blue.

8. A "wool" blue (triphenylmethane group).

9. A dyestuff of the "patent blue" class, such as patent blues V A,

or N, Cyanol, Cyanine, Ketone Blues, Erioglaucine, etc. (triphenylmethane group).

10. A soluble or alkali blue (Rosaniline Blue).

11. An acid azo blue, such as Lanacyl Blue, Azo Acid Blue, Azo Merino Blue, Azo Navy Blue, etc.

12. Acid Alizarin Blues (without mordant), such as Alizarin Saphirol, Alizarin Irisole, Alizarin Astrole.

13. A salt dyestuff, such as Diamine, Benzo, Chicago or Dianil Blues, Sulphone Cyanines, etc.

14. Indigo.

15. An Alizarin Cyanine or Anthracene Blue.

16. An Alizarin Blue (anthraquinonequinolines).

17. Brilliant Alizarin Blue (thiazine group).

18. Gallocyanines, Gallamine Blue, Celestine Blue, Prune, etc. (oxazine group).

19. Chrome Blue (triphenylmethane group).

20. A mordant azo dyestuff, such as Cyprus Blue, Peri Wool Blue, Anthracene Chrome Blue, Chromotrope Blue, etc.

Examination of Green Shades.

(See Table V.)

Green shades are frequently dyed with mixtures of yellow and blue dyestuffs (see Tables I and IV). The following single dyestuffs also come into consideration:

1. A basic safranine-azo colour, such as Janus Green or Diazine Green.

2. A basic azine, thiazine, or oxazine, such as Fast Green M, Azine Green, Capri Green, Methylene Green, etc.

3. A basic triphenylmethane dyestuff, such as Malachite Green, Methyl Green, Brilliant or Ethyl Green, Solid Green, Setoglaucine, etc.

4. An acid azine, oxazine, or thiazine, such as Azine Green S.

5. An acid triphenylmethane dyestuff, such as Acid Green, Light Green, Guinea Green, Wool Green, Neptune Green, Naphthalene Green, etc.

6. An acid azo colour, *e.g.*, a mixture of an Azo Blue and an Azo Yellow.

7. A salt dyestuff, such as Diamine Green, Columbia Green, Chloramine Green, Benzo Green, etc.

8. Cœruleïn, Alizarin Green S.

9. Alizarin Cyanine Greens, Alizarin Viridine.

10. Alizarin Green G or B (oxazine group).

11. Nitroso mordant dyestuffs, *e.g.*, Gambine Y, R, and B, Dioxine, Dark Green, and Naphthol Green.

12. Azo mordant dyestuffs, such as Diamond Green and Chrome Patent Green.

Examination of Brown Shades.

(See Table VI.)

Brown shades are usually dyed with mixtures of dyestuffs, such as reds, oranges, blues, and greens. Even the brown dyestuffs issued by the colour manufacturers are to a large extent mixtures. The following scheme is applicable to single dyestuffs or to mixtures composed of two or more dyestuffs of the same group. If dyestuffs of different groups are present (*i.e.*, an azo orange with a blue of the triphenylmethane series), the respective tables must be consulted. The following single dyestuffs come into consideration:

1. Basic browns, such as Bismarck Brown or Vesuvine.

2. Acid azo colours, such as Acid Brown R, Fast Brown O, Resorcin Brown, Naphthylamine Brown, etc.

3. Salt dyestuffs of the azo group, such as Diamine Browns, Benzo Browns, Congo Browns, Hessian Browns, Columbia Browns, Tolylene Browns, Dianil Browns, Sulphone Browns, etc.

4. Salt dyestuffs of the stilbene group, *e.g.*, Mikado Browns.

5. Anthragallol (Anthracene Brown).

6. Cutch.

7. Chromogen.

8. Mordant azo colours, such as Anthracene Acid Browns, Acid Anthracene Brown, Palatine Chrome Brown, Acid Chrome Brown, Diamond Brown, Metachrome Brown, etc. Also Manganese Brown.

Examination of Blacks and Greys.

(See Table VII.)

The fibre may be dyed by one of the following:

1. A basic black or grey, such as Diazine Black, Janus Black, Methylene Grey, etc.

2. An acid black, such as Naphthol Black, Naphthylamine

Black, Palatine Black, Nerol, Anthracene Black, Azo Acid Black, Azo Merino Black, etc.

3. A salt dyestuff, such as Union Black, Half-wool Black, Columbia Black, Diamine Blacks, Dianil Blacks, Carbide Blacks, etc.

4. A mordant azo dyestuff, such as Anthracene Chrome Blacks, Palatine Chrome Black, Chromotropes, Chromate Black, Acid Chrome Blacks, etc.

5. A "vatted" black (indigo and logwood).

6. Logwood black on chromium mordant.

7. Logwood black on iron mordant or Bonsor's black.

8. Naphthazarin, Alizarin Blacks, or Alizarin Blue Black SW (naphthoquinone group).

9. Diamond Blacks.

10. Alizarin Cyanine Black (anthraquinone group).

11. Aniline black.

Mixtures.—If a mixture consists of two or more dyestuffs of the same chemical and dyeing group, it will behave as a whole similarly to a single dyestuff, though sufficient differences may exist in the rate of solution or of attack by the group reagents to render it possible to distinguish or even to separate the constituents. Thus a green consisting of a mixture of an acid Azo Yellow with an Acid Azo Blue will be distinguishable upon careful reduction with hydrosulphite, since the Azo Blue will be reduced first, and the shade will therefore change from green to yellow before it is decolourised. Neither colour will return on oxidation. Further, if such a compound shade be extracted fractionally with dilute ammonia, the yellow is generally stripped first, and may be transferred to another piece of wool for subsequent tests. Mixtures of colours belonging to different groups will usually exhibit at once their diverse composition. For example, a navy blue shade dyed with Patent Blue and an Azo Orange will, upon reduction, first change to bright blue, then become colourless, and upon reoxidation with persulphate the blue alone will return. If a mixture of an azine, oxazine, or thiazine dyestuff with a triphenylmethane colour has been employed, only the first will return upon exposure of the leuco-compound to air, the latter being also restored upon treatment with persulphate. Fractional extraction of the fibre with dilute alcohol or dilute acetic acid can also be employed in many cases to effect a separation or partial separation of the dyestuffs, the extracted colour being then transferred to fresh wool or silk and separately tested.

TABLE I.—YELLOW AND ORANGE COLOURS.

<table>
<tr><td colspan="9">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td colspan="4">Much colour is stripped: Basic dyestuff. Boil with hydrosulphite B.</td><td colspan="5">Little or no colour is stripped: Acid, salt, or mordant dyestuff. Boil twice for 1 minute with dilute ammonia (1:100) and a piece of white cotton. Keep the ammoniacal extract.</td></tr>
<tr><td colspan="3">Not decolourised or only very slightly. Treat fibre with conc. H_2SO_4.</td><td rowspan="3">Decolourised. Colour is not restored by air or by persulphate: Azo-group.</td><td colspan="5">Much colour is stripped but cotton remains white: Acid dyestuff. Boil with hydrosulphite B.</td></tr>
<tr><td rowspan="2">Green fluorescent solution: Acridine group.</td><td colspan="2">Colourless solution. Boil with dilute HCl (1:10).</td><td rowspan="2">Colour is not affected: Quinoline or Pyrone group.</td><td colspan="4">Decolourised, and colour dces not return on exposure to air or upon oxidation with persulphate: Azo group or Nitro group. Add conc. HCl to the ammoniacal extract.</td></tr>
<tr><td>Completely decolourised</td><td>Fibre and solution pale yellow</td><td>No change of colour</td><td>Becomes colourless</td><td>Becomes red</td><td>Becomes violet or violet red</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td></tr>
<tr><td>Phosphine, Benzoflavine, Rheonine, Acridine Orange, etc.</td><td>Auramine.</td><td>Thioflavine T.</td><td>Chrysoidine, Tannin Orange, Janus Yellow.</td><td>Quinoline Yellow, Uranine, Eosin Orange.</td><td>Tartrazin, Oranges G, 2G, R, etc.</td><td>Naphthol Yellow S, Martius Yellow.</td><td>Fast Yellow, Indian Yellow, Azoflavine, etc.</td><td>Metanil Yellow, Orange IV.</td></tr>
</table>

TABLE I.—YELLOW AND ORANGE COLOURS.—*Continued.*

Boil twice for 1 minute with 5% acetic acid.					
Little or no colour is stripped: **Acid, salt, or mordant dyestuff.** Boil twice for 1 minute with dilute ammonia (1 : 100) and a piece of white cotton. Keep the ammoniacal extract.					
Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is tinted (salt dyestuff). Boil with 5% sodium acetate and white cotton for 2 or 3 minutes.					
The cotton is stained: **Salt dyestuff.** Boil with hydrosulphite B.			The cotton remains white: **Mordant dyestuff.** (Confirm by testing ash for metallic mordants.) Boil with hydrosulphite B.		
Not affected or slightly changed in shade: **Thiazole group.**	Decolourised. Colour restored by exposure to air or more quickly by persulphate: **Stilbene group.**	Decolourised. Colour not restored by air or by persulphate: **Azo group.**	Not affected: **Flavone and ketone group.**	Colour changed to yellowish brown: **Alizarine group.**	Decolourised and colour not restored by air or persulphate: **Azo group.**
10	11	12	13	14	15
Thioflavine S, Chloramine Yellow, Chlorophenine, Thiazole Yellow, etc., also turmeric.	Curcumin S, Mikado Yellows and Oranges, Stilbene Yellows, etc.	Chrysophenin Yellow, Benzo, Congo, or Diamine Oranges, etc.	Fustic, Quercitron, weld,[1] Alizarin Yellow A, etc.	Alizarin Orange.	Alizarin Yellows G and R, Anthracene Yellow C, Flavazol, Chrome Orange, etc.

[1] Weld is partly discharged by acetic acid though the solution remains colourless.

TABLE II.—RED COLOURS.

<table>
<tr><td colspan="14">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td colspan="5">The colour is stripped: Basic dyestuff or soluble red woods. Boil with dilute alcohol (1 : 1) twice for 1 minute.</td><td colspan="9">Little or no colour is stripped: Acid, salt, or mordant dyestuffs. Boil twice for 1 minute with dilute ammonia (1:100) and a small piece of white cotton. Keep the ammoniacal extract.</td></tr>
<tr><td colspan="4">Much of the colour is stripped: Basic dyestuff. Boil with hydrosulphite A.</td><td rowspan="4">Unaffected. Al or Cr are present in ash. Boiling with dilute ammonia renders the colour much bluer.</td><td colspan="9">Much colour is stripped but cotton remains white: Acid dyestuff. Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="3">Colour not affected.</td><td rowspan="3">Decolourised. Colour returns quickly on exposure to air.</td><td rowspan="3">Decolourised. Colour does not return on exposure to air but is restored by persulphate.</td><td rowspan="3">Decolourised. Colour is not restored either by air or by persulphate.</td><td colspan="2">Colour of wool not altered: Pyrone group. Acidify the ammoniacal extract.</td><td rowspan="3">Decolourised. Colour returns on exposure to air: Azine group.</td><td rowspan="3">Decolourised. Colour does not return on exposure to air but is restored by persulphate: Triphenylmethane group.</td><td colspan="5">Decolourised. Colour not restored either on exposure to air or on oxidation with persulphate: Azo group. Boil with dilute dichromate.</td></tr>
<tr><td rowspan="2">Precipitation and disappearance of fluorescence.</td><td rowspan="2">No pp. and fluorescence remains.</td><td colspan="4">Colour unaffected. Evaporate ammoniacal extract and dissolve in conc. H_2SO_4.</td><td rowspan="2">Changes to dark maroon or violet black.</td></tr>
<tr><td>Red solution</td><td>Violet solution</td><td>Blue solution</td><td>Green solution</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td colspan="5">10</td></tr>
<tr><td>Basic dyestuff of pyrone group.</td><td>Basic dyestuff of azine group.</td><td>Basic dyestuff of triphenylmethane group.</td><td>Basic azo dyestuff, e.g., Janus Red.</td><td>Soluble red woods.</td><td>Eosin, Phloxin Erythrosin, etc.</td><td>An acid Eosin, or acid rhodamine.</td><td>Azocarmine or rosinduline</td><td>Acid Magenta.</td><td>Xylidine or Palatine Scarlet.</td><td>Crystal Scarlet, Fast Red A, etc.</td><td>Crocein Scarlet, Fast Red B, etc.</td><td>Biebrich Scarlet, etc.</td><td>Chromotropes. Azofuchsine, etc.</td></tr>
</table>

TABLE II.—RED COLOURS.—*Continued.*

Boil twice for 1 minute with 5% acetic acid.											
Little or no colour is stripped: **Acid, salt, or mordant dyestuffs.** Boil twice for 1 minute with dilute ammonia (1 : 100) and a small piece of white cotton. Keep the ammoniacal extract.											
Some of the colour is stripped and the wool becomes much bluer. Boil with hydrosulphite A.		Little or no colour is stripped. The cotton remains white (mordant dyestuffs), or is stained (salt dyestuffs). Both with 5% sodium acetate and white cotton for 2 or 3 minutes.									
Colour slowly changed to deep yellow. Original colour not restored on exposure to air.	Decolourised. Colour is quickly restored on exposure to air.	The cotton is stained: **Salt dyestuff.** Test ash for chromium.						The cotton remains white: **Mordant dyestuff.** (Confirm by testing ash for metallic mordants). Boil with hydrosulphite A.			
		Chromium is absent. Treat fibre with conc. sulphuric acid.					Cr is present. Solution in conc. H_2SO_4 is red.	Colour not affected. Al in ash.	Colour slowly changed to yellow or orange. Al in ash.	Decolourised. Colour is restored by persulphate. Al in ash.	Decolourised. Colour is not restored by persulphate. Cr in ash.
		Crimson red solution	Violet red solution	Violet solution	Blue solution	Greenish-blue solution					
11	12	13						14	15	16	17
Cochineal Scarlet.	Archil.	Rosophenine.	Erica or Geranin.	Diamine. Scarlet.	Diamine Fast Red.	Hessian Purple.	Anthracene Red.	Cochineal Crimson.	Alizarin Reds.	Insoluble red woods.	Mordant azo colour.

TABLE III.—PURPLE AND VIOLET COLOURS.

<table>
<tr><td colspan="8">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td colspan="2" rowspan="2">Colour is nearly completely stripped: Basic dyestuff. Boil with hydrosulphite A.</td><td colspan="6">The colour is not stripped: Acid, salt, and mordant dyestuffs. Boil twice for 1 minute with aqueous alcoholic ammonia and white cotton.</td></tr>
<tr><td colspan="6">Much colour is stripped but cotton remains white: Acid dyestuff. Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="3">Decolourised. The colour returns on exposure to air.</td><td rowspan="3">Decolourised. The colour only returns on oxidation with persulphate.</td><td rowspan="3">Not altered or only partially decolourised: Pyrone group.</td><td colspan="3">Decolourised. The colour does not return on exposure to air, but is restored upon oxidation with persulphate: Triphenylmethane group.</td><td rowspan="3">Decolourised. The colour returns on exposure to air: Azine, oxazine or thiazine group.</td><td rowspan="3">Decolourised. The colour is not restored either by exposure to air or by oxidation with persulphate: Azo group.</td></tr>
<tr><td rowspan="2">The ammoniacal extract is violet or purple.</td><td colspan="2">The ammoniacal extract is colourless, but becomes violet on acidifying. Spot fibre with conc. HCl.</td></tr>
<tr><td>Becomes green</td><td>No change</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td></tr>
<tr><td>Basic violet of the azine, oxazine, or thiazine groups.</td><td>Basic violet of triphenylmethane group, e.g., Methyl Violet.</td><td>Fast Acid Violets or Violamines.</td><td>Acid Violets. Formyl Violets, etc.</td><td>Alkali Violet.</td><td>Red shade Soluble Blues.</td><td>Induline or Fast Blue R, etc.</td><td>Lanacyl Violet, Victoria Violet, etc.</td></tr>
</table>

TABLE III.—PURPLE AND VIOLET COLOURS.—*Continued.*

<table>
<tr><td colspan="7">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td colspan="7">The colour is not stripped: Acid, salt, and mordant dyestuffs. Boil twice for 1 minute with aqueous alcoholic ammonia and white cotton.</td></tr>
<tr><td colspan="7">Little or no colour is stripped. The cotton remains white (mordant dyestuffs) or is tinted (salt dyestuffs). Boil with sodium acetate and white cotton for 2 or 3 minutes.</td></tr>
<tr><td rowspan="3">The cotton is stained: Salt dyestuff.</td><td colspan="6">The cotton remains white. Mordant colour. (Confirm by testing for metallic mordants in ash.) Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="2">Colour not altered: Pyrone group.</td><td colspan="2">Colour changed to brown: Alizarin group. Boil with dilute HCl.</td><td rowspan="2">Decolourised. Colour returns on exposure to air.</td><td rowspan="2">Decolourised. Colour does not return on exposure to air, but is restored by oxidation with persulphate.</td><td rowspan="2">Decolourised. Colour is not restored either by exposure to air or by oxidation with persulphate.</td></tr>
<tr><td>Fibre and solution yellow</td><td>Fibre and solution red or reddish-brown</td></tr>
<tr><td>9
Hessian Violet, Diamine Violet, etc.</td><td>10
Gallein.</td><td>11
Alizarin on Fe[1] or Cr.</td><td>12
Alizarin Bordeax.</td><td>13
Gallocyanin, Prune, Celestin Blue, etc.</td><td>14
Chrome Violet.</td><td>15
Mordant azo colour.</td></tr>
</table>

[1] Alizarin on iron becomes brown on boiling with 5% acetic acid.

TABLE IV.—BLUE COLOURS.

<table>
<tr><td colspan="12">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td colspan="4">Much colour is stripped. Boil with dilute alcohol (1:1) twice for 1 minute.</td><td colspan="8">Little or no colour is stripped: Acid, salt, or mordant dyestuff. Boil twice for 1 minute with dilute ammonia (1:100) and small piece of white cotton. Keep the ammoniacal extract.</td></tr>
<tr><td colspan="3">Much colour is stripped: Basic dyestuff. Boil with hydrosulphite A.</td><td rowspan="4">Unaffected. Al or Cr or both are present in ash. The blue is changed to brick red on spotting with HCl.</td><td colspan="8">Much colour is stripped but cotton remains white: Acid dyestuff. Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="3">Decolourised. Original colour returns on exposure to air: Azine, oxazine, or thiazine group.</td><td rowspan="3">Decolourised A violet colour returns on exposure to air: Safranine azo colour.</td><td rowspan="3">Decolourised. The colour does not return on exposure to air but is restored by persulphate: Triphenylmethane group.</td><td colspan="3">Decolourised and colour restored on exposure to air: Azine, oxazine, thiazine, and indigo group. Also Prussian blue.</td><td colspan="3">Decolourised. Colour does not return on exposure to air but is restored by persulphate: Triphenylmethane group.</td><td rowspan="3">Decolourised. Colour is not restored either by air or by persulphate: Azo group.</td><td rowspan="3">Not decolourised but colour changed to bluish-red: Alizarin group.</td></tr>
<tr><td colspan="2">Ammon. extract is blue and on adding NaOH.</td><td rowspan="2">Ammon. extract is colourless. Fe in ash.</td><td colspan="2">Ammon. extract is blue. On boiling with NaOH it becomes</td><td rowspan="2">Ammon. extract is colourless but becomes blue on acidifying.</td></tr>
<tr><td>at once becomes yellow.</td><td>becomes violet on heating.</td><td>colourless.</td><td>violet.</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td></tr>
<tr><td>Methylene Blue, Nile Blue, Capri Blue, etc.</td><td>Indoine or Janus Blue.</td><td>Victoria Blue, Night Blue, etc.</td><td>Logwood Blue.</td><td>Indigo extract.</td><td>Thiocarmine.</td><td>Prussian blue.</td><td>A "wool" blue.</td><td>A "patent" blue.</td><td>A "soluble" or "alkali" blue.</td><td>An Acid Azo Blue, e.g. Lanacyl Blue.</td><td>Alizarin Saphirole, Alizarin Astrole, etc.</td></tr>
</table>

TABLE IV.—BLUE COLOURS.—*Continued.*

<table>
<tr><td colspan="8">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td colspan="8">Little or no colour is stripped: Acid, salt, or mordant dyestuff. Boil twice for 1 minute with dilute ammonia (1:100) and small piece of white cotton. Keep the ammoniacal extract.</td></tr>
<tr><td colspan="8">Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is tinted (salt dyestuff). Boil with 5% sodium acetate and white cotton for 2 or 3 minutes.</td></tr>
<tr><td rowspan="4">The cotton is stained: Salt dyestuff. On reduction with hydrosulphite A the colour is not restored either by air or persulphate: Azo group.</td><td colspan="7">The cotton remains white. Boil with a little aniline oil.</td></tr>
<tr><td rowspan="3">Blue solution which on evaporation to dryness leaves a residue which sublimes in violet vapours on heating.</td><td colspan="6">The solution is light brown or colourless: Mordant dyestuff. Confirm by testing ash for metallic mordants. Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="2">Colour of wool unaltered: Alizarin group.</td><td rowspan="2">Colour changed to dark brown becoming blue again on exposure to air: Aliz. group.</td><td colspan="2">Decolourised, but colour returns on exposure to air: Oxazine or thiazine group. Treat fibre with conc. H_2SO_4.</td><td rowspan="2">Decolourised. Colour does not return on exposure to air, but is restored by persulphate: Triphenylmethane group.</td><td rowspan="2">Decolourised. Colour is not restored either by air or persulphate: Azo group.</td></tr>
<tr><td>Green solution.</td><td>Violet solution.</td></tr>
<tr><td>13</td><td>14</td><td>15</td><td>16</td><td>17</td><td>18</td><td>19</td><td>20</td></tr>
<tr><td>Diamine or Benzo Blues, etc.</td><td>Indigo.</td><td>An Alizarin, Cyanine, or Anthracene Blue.</td><td>An Alizarin Blue (anthraquinonequinoline).</td><td>Brilliant Alizarin Blue</td><td>Gallocyanines, Celestine Blue, etc.</td><td>Chrome Blue.</td><td>A mordant azo blue.</td></tr>
</table>

TABLE V.—GREEN COLOURS.

Boil twice for 1 minute with 5% acetic acid.

The colour is stripped: **Basic dyestuff.** Boil with hydrosulphite A.			The colour is not stripped: **Acid, salt,** or **mordant dyestuff.** Boil twice for 1 minute with dilute ammonia (1 : 100) and a small piece of white cotton.		
			Much colour is stripped but the cotton remains white: **Acid dyestuff.** Boil with hydrosulphite A.		
Decolourised. A dark violet colour returns on exposure to air: **Safranine azo colour.**	Decolourised. Original colour returns on exposure to air: **Azine, oxazine** or **thiazine group.**	Decolourised. The colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane group.**	Decolourised. Colour returns on exposure to air: **Azine, oxazine** or **thiazine group.**	Decolourised. Colour does not return on exposure to air but is restored by persulphate: **Triphenylmethane group.**	Decolourised. Colour is not restored either by air or persulphate: **Azo group.**
1	2	3	4	5	6
Janus Green or Diazine Green.	Fast Green M, Azine Green, Capri Green, etc.	Malachite Green, Brilliant Green, Seto-glaucine, etc.	Azine Green S.	Acid Greens, Light Greens, Guinea Green, Wool Green, etc.	Chiefly mixtures of an Azo Blue and Yellow.

TABLE V.—GREEN COLOURS.—*Continued.*

Boil twice for 1 minute with 5% acetic acid.

The colour is not stripped: **Acid, salt,** or **mordant dyestuff.** Boil twice for 1 minute with dilute ammonia (1 : 100) and a small piece of white cotton.

Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is stained (salt dyestuff). Boil for 2 or 3 minutes with 5% sodium acetate and a piece of white cotton.

The cotton is deeply stained: **Salt dyestuff.**	The cotton remains white:[1] **Mordant dyestuff.** Confirm by testing for metallic mordant in ash. Boil with hydrosulphite A.				
	Colour changes to brown: **Alizarine group.**		Decolourised (or changed to light buff).		
	Original colour returns on exposure of air.	Original colour does not return on exposure to air but is restored by persulphate.	Colour returns on exposure to air: **Oxazine** or **thiazine group.**	Colour does not return on exposure to air or upon oxidation with persulphate: **Nitroso** or **Azo group.** Boil with conc. hydrochloric acid.	
				Fibre and solution light brown: **Nitroso group.**	Fibre blue and solution colourless: **Azo group.**
7	8	9	10	11	12
Diamine Green, Columbia Green, Chloramine Green, etc.	Cœrulein or Alizarin Green S.	Alizarin Cyanin Green or Alizarin Viridine.	Alizarin Green G or B (D).	Gambines, Dioxine, Dark Green, Naphthol Green.	Diamond Green, Chrome Patent Green, etc.

[1] With azo mordant colours the cotton may be slightly tinted, especially if the fixation by chrome is not complete.

TABLE VI.—BROWN COLOURS.

<table>
<tr><td colspan="8">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td rowspan="5">Much colour is stripped: Basic dyestuff. On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate: Azo group.</td><td colspan="7">Little or no colour is stripped: Acid, salt, or mordant dyestuff. Boil twice for 1 minute with dilute ammonia.</td></tr>
<tr><td rowspan="4">Much colour is stripped: Acid dyestuff. On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate: Azo group.</td><td colspan="6">Little or no colour is stripped: Salt or mordant dyestuff. Boil for 2 to 3 minutes with 5% sodium acetate and white cotton.</td></tr>
<tr><td colspan="2">The cotton is stained: Salt dyestuff. Boil with hydrosulphite A.</td><td colspan="4">The cotton remains white: Mordant dyestuff. Confirm by testing for metallic mordants in ash. Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="2">Decolourised, but colour not restored by air or persulphate: Azo group. Test ash for chromium to ascertain if chromed (Cloth Brown, Chrome Brown, etc.)</td><td rowspan="2">Decolourised, but colour returns slowly on exposure to air or quickly on oxidation with persulphate: Stilbene group.</td><td colspan="2">Colour not changed. Boil with dilute hydrochloric acid (1:10).</td><td colspan="2">Decolourised or changed to pale buff or light brown.</td></tr>
<tr><td>Colour is stripped.</td><td>Colour not stripped.</td><td>Colour returns slowly on exposure to air or quickly on oxidation with persulphate.</td><td>Colour not restored either by air or persulphate: Azo group.</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td></tr>
<tr><td>Bismarck Brown.</td><td>Acid Brown R, Fast Brown O, etc.</td><td>Diamine Browns, Benzo Browns, Tolylene Browns, etc.</td><td>Mikado Browns.</td><td>Anthragallol (Anthracene Brown).</td><td>Cutch.</td><td>Chromogen.</td><td>Anthracene Acid Browns, Acid Anthracene Brown, Palatine Chrome Brown, etc., also Manganese Brown (Mn in ash).</td></tr>
</table>

TABLE VII.—BLACK AND GREY COLOURS.

<table>
<tr><td colspan="11">Boil twice for 1 minute with 5% acetic acid.</td></tr>
<tr><td rowspan="6">Much colour is stripped: Basic dyestuff. (N. B.—Logwood black on Fe mordant also becomes much paler though solution is not coloured.)</td><td colspan="10">The colour is not stripped: Acid, salt, or mordant dyestuff. Boil twice for 1 minute with aqueous alcoholic ammonia and small piece of white cotton.</td></tr>
<tr><td rowspan="5">Much colour is stripped but the cotton remains white: Acid dyestuff. On boiling with hydrosulphite A the colour is permanently discharged.</td><td colspan="9">The colour is not stripped: Salt and mordant dyestuffs. Boil with 5% sodium acetate and small piece of white cotton.</td></tr>
<tr><td colspan="2" rowspan="2">The cotton is stained: Salt and azo mordant dyestuff. Permanently decolourised by hydrosulphite A. Test ash for chromium.</td><td colspan="7">The cotton remains white: Mordant dyestuffs. (Confirm by testing ash for mordant.) Boil with dilute hydrochloric acid (1:10).</td></tr>
<tr><td rowspan="3">Fibre blue and solution crimson. Test for indigo by boiling with a little aniline: blue solution, which on evaporation to dryness gives residue subliming in violet vapour.</td><td rowspan="3">Fibre and solution crimson</td><td rowspan="3">Fibre and solution pale brown.</td><td colspan="4">Not affected. Boil with hydrosulphite A.</td></tr>
<tr><td rowspan="2">Cr. is absent: Salt dyestuffs.</td><td rowspan="2">Cr. is present: Mordant azo dyestuffs.</td><td rowspan="2">Becomes brown. Original colour slowly returns on exposure to air.</td><td rowspan="2">Decolourised. Colour is not restored by exposure to air or by persulphate</td><td colspan="2">Unaffected. Treat fibre with conc. H_2SO_4.</td></tr>
<tr><td>Blue solution.</td><td>Colourless solution.</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td></tr>
<tr><td>Diazine Black, Janus Black, Methylene Grey, etc.</td><td>Naphthol Black, Naphthylamine Black, Palatine Black, etc.</td><td>Union Black, Half-Wool Black, Columbia Black, etc.</td><td>Anthracene Chrome Blacks, Palatine Chrome Black, Chromotropes, etc.</td><td>A "vatted black" (indigo and logwood).</td><td>Logwood on Cr.</td><td>Logwood on Fe, or Bonsor's Black.</td><td>Naphthazarin, Alizarin Black S, Alizarin Blue Black SW.</td><td>Diamond Blacks.</td><td>Alizarin Cyanine Black.</td><td>Aniline Black.</td></tr>
</table>

Recognition of the Constituents Dyes of Compound Shades.—The following hints, chiefly by G. Dommerque (*Monit. Scient.*, 1889, **33**, 25), may be given as an example of the methods which have been adopted for identifying the constituents of mixed dyes on wool.

Garnet shades contain red as the predominating constituent. Bright garnets are a mixture of yellow and red. In examining them, moisten the fibre with hydrochloric acid. If turned yellow, the yellow constituent was Manchester Yellow (dinitro-cresol), this being the only yellow which is dyed in a neutral bath, and which does not precipitate the salts of rosaniline. If on application of hydrochloric acid the shade becomes slightly bluer, the colour is possibly produced from Acid-Magenta and Naphthol-Yellow or Chrysoïn; while if it turn Violet, Acid-Magenta and orange IV (or an allied orange or yellow azo-dye) are indicated. Some bright garnet shades lose their red colour when moistened with ammonia, yellow remaining. The rarely occurring shades produced with Bordeaux and Amaranth are not altered by ammonia, but become violet-blue or blue when touched with sulphuric acid.

Maroons and compound-red shades are examined by moistening the fibre with ammonia. If it become green, the fibre was probably dyed with a mixture of Acid-Magenta and sulphonated indigo. If turned yellow, the same portion of fibre should be slightly washed and treated with hydrochloric acid, when if the yellow become violet, Orange IV or other azo-orange or yellow is indicated; while if rendered slightly blue, Chrysoïn or Naphthol-Yellow is the probable yellow constituent. If the yellow colour produced by ammonia remain unchanged on subsequent treatment with hydrochloric acid, the presence of Acid Green, Acid-Violet, and Acid-Magenta is probable. If Orange IV be also present, the fibre becomes reddish-violet with hydrochloric acid. If the colour be unaffected, or simply rendered paler by treatment with ammonia, the dye may be either a mixture of an azo-red, indigo and Orange IV, in which case it becomes slightly violet with hydrochloric acid (if this acid produces no change, Chrysoïn is probably present); or logwood, becoming red with hydrochloric acid. If dyed with a mixture of logwood and Orange IV, acid changes the colour to violet-red or garnet.

Scarlets.—Cochineal-scarlets are turned violet by alkali hydroxides, and the ash contains tin; alkalies turn some artificial scarlets yellow.

Dark Blues and Purples.—Complete decolourisation on moistening

the fibre with ammonia points to a probable mixture of Acid-Green, Acid-Violet, and Acid-Magenta. If the red be removed from the fibre and the blue left, the latter is probably indigo and the former Acid-Magenta. If the shade become slightly pale the dye is probably a mixture of indigo and an azo-red, in which case the shade will not be appreciably changed on further testing the fibre with hydrochloric and sulphuric acid. Logwood will colour the acid red, and the ash will contain chromium. In shades produced by mixtures of logwood, sulphonated indigo, and Acid-Magenta or an azo-red, the constituents are difficult to identify.

Dark Greens.—If only the yellow remain on moistening the tissue with ammonia, a mixture of Acid-Green and Acid-Violet with Naphthol-Yellow may be suspected. Should the shade if changed become paler, the fibre is moistened with hydrochloric acid, when logwood will colour the acid red. If the fibre becomes red or violet-red and the ash contains chromium, the yellow constituent is probably fustic. If, on treatment with the acid, the yellow disappears and the blue remains, a mixture of indigo with Naphthol-Yellow may be present.

Olives, when moistened with ammonia, turn yellow if dyed with a mixture containing Acid-Green and Acid-Violet, and on treating the fibre with hydrochloric acid it will become garnet if the yellow constituen tbe Orange IV, and yellow-brown if it be Chrysoïn. Olives containing indigo become slightly bluer with ammonia.

Mode colours are liable to contain a great variety of dyes, perhaps the most common being Orchil-substitutes (azo-reds), azo-oranges, and Acid-Magenta.

Tables of Reactions of Dyed Fibres.

The following tables, originally given by B. Martinon (*Soc. Dyers*, 3, 124) for the recognition of dyes on silk, involve the use of certain reagents, such as a solution of bleaching powder and nitrous acid, which are not in such general use. The reagents employed are:

Sodium Hydroxide Solution.—1 part in 10 of water.

Hydrochloric Acid.—Acid of 1.16 sp. gr. diluted with an equal volume of water.

Calcium Hypochlorite.—40 grm. of bleaching powder dissolved in 1 litre of water and the liquid filtered.

Nitrous Acid.—20 grm. of sodium nitrite and 15 grm. of sulphuric acid (sp. gr. 1.845) are respectively dissolved in 1 litre of water. Equal volumes of these solutions are mixed when required.

Potassium Cyanide.—50 grm. in 1 litre of water.

Nitric Acid.—Acid of 1.32 sp. gr. diluted with an equal volume of water.

Sodium Carbonate.—1 part of the salt in 10 parts of water.

From 10 to 15 c.c. of the required reagent should be placed in a porcelain dish, the silk to be tested immersed in it, and the change of colour observed. After 2 or 3 minutes, the silk is taken out and well washed. Another portion of the silk should be simultaneously placed in clear water, in order that any change in colour by the action the reagent may be better observed. To ensure absolute certainty, it is also advisable to dye a piece of clean silk with the detected dye, and to repeat the experiments on this from the beginning.

G. Dommerque has published (*J. Soc. Chem. Ind.*, **8**, 216) a systematic method of recognising dyes on wool. In some cases different observers have given different reactions for the same dyestuff; and, on the whole, the reactions for dyes on the fibres are still in rather an unsatisfactory and uncertain condition, leaving much to be desired in this direction. The results obtained should always be checked by comparison with the suspected dye or dyes.

The tables of Hummel, Lehne and others, already referred to, together constitute the most complete description of the reactions of dyes on fibres yet compiled, and as the present section would be imperfect if these reactions were omitted, they are given in a compilation with a few modifications from the above references in the following pages.

YELLOW DYES—ON SILK.

HCl						Dye
No action.	NaOH	No action. HNO₃ →	Green-yellow, then dirty green. On washing, slowly faint yellow			Saffron.
			Faint brown; on washing again yellow			Quinoline Yellow.
		Alters shade slightly	Alkaline liquid brownish-yellow, with faint green fluorescence	HNO₃ and washing	No action	Fustic and SnO_2.
					Brownish-yellow	Fustic and Al_2O_3.
		Brown-yellow	The alkaline liquid is yellow. With HNO_3 silk becomes yellowish-brown			Quercitron and SnO_2.
			$CaOCl_2$	Brown; with HNO_3 brownish-yellow		Sumac and Al_2O_3.
				Brown; with HNO_3 chestnut-brown		Alkanet.
		Reddens somewhat. $CaOCl_2$ without action				Heliochrysin.
		Turns red and then decided brown; on washing again yellow. With HNO_3 more yellow				Nitro-alizarin.
		Faint greenish-yellow. $CaOCl_2$ decolourises. On washing remains a faint yellow colour				Phosphine.
		Pure Yellow. $CaOCl_2$ bleaches silk slowly				Chrysoïdine.
	H_2O	Bleached on washing. $CaOCl_2$ without action				Quercitron and Al_2O_3.
		Bleached by washing, and remains brown-yellow. With $CaOCl_2$ silk becomes brown-yellow				Weld and Al_2O_3.
Decolourises or bleaches considerably	NaOH	Decolourises	Colour does not return after washing			Chrome Yellow.
			Colour reappears on washing	Na_2CO_3 without action		Auramine.
				Na_2CO_3 decolourises		Flavin.
		Reddens				Aurantia.
		Changes slowly into orange-yellow. With KCy	Reddish-yellow			Picric acid.
			No action			Naphthol Yellow S
		Scarlet				Chrysamine.
Intense red.	HCl coloured violet-red. With water silk turns brownish-red, then again yellow					Orange IV.
Reddish-brown.	NaOH	The silk becomes reddish-brown. HNO_3 without action				Turmeric.
		The NaOH is coloured orange. HNO_3 chestnut-brown				Young fustic.
Dark yellowish-brown colour; on washing it remains a brownish-yellow. With NaOH chestnut-brown, with $CaOCl_2$ orange						Alkanet and Al_2O_3.
Reddish; with NaOH chestnut-brown. $CaOCl_2$ and HNO_3 without action						Citronin.
Orange. NaOH faint brown. With $CaOCl_2$ colour becomes slightly red						Amidoazobenzene.
Orange; with NaOH scarlet. $CaOCl_2$ wood colour. With HNO_3 reddish-brown						Chrysoin.

ORANGE YELLOW DYES—ON SILK.

HCl	Without action	NaOH	No action	Turmeric.
			Reddens and turns decided brown. HNO_2 without action	Nitroalizarin.
	Scarlet, more or less brownish	NaOH	Scarlet	Orange I and II.
			Pure Yellow	Orange III.

RED DYES.

HCl	No action	NaOH	Turns some what brown	Roccellin.
			Violet-red; HNO_2: No action; HNO_3: Brownish-red	Magdala Red.
			Violet-red; HNO_2: No action; HNO_3: Reddish-violet	Archil substitute.
			The silk becomes violet; HNO_2: Bleached and turned yellow	Archil.
	Bluish-violet	NaOH	Scarlet. $CaOCl_2$ no action	Congo Red.
			Pale violet-red. $CaOCl_2$ decolourises	Safranine.
	Reddish-violet.	NaOH decolourises		Acid Magenta.
		NaOH	Decolourises slowly; silk remains faint rose-colour, and becomes red on washing	Magenta.
			No action	Benzopurpurin.
			Silk becomes lilac	Ammoniacal Cochineal.
	Bright yellow	NaOH	Violet-red; $CaOCl_2$; Na_2CO_3: No action. Solution in boiling alcohol is fluorescent	Eosin.
			Violet-red; $CaOCl_2$; Na_2CO_3: The Na_2CO_3 becomes pale violet	Erythrosin.
			Violet-red; $CaOCl_2$: First violet, then slowly loses color	Cochineal.
			Violet-red; $CaOCl_2$: No action. The Na_2CO_3 becomes violet	Alizarin.
			Silk decolourised; the sodium hydroxide solution is coloured brownish-red	Safrosin.
	Silk more or less brownish-yellow	NaOH	No action; HNO_2: No action	Silk Scarlet.
			No action; HNO_2: Wood colour	Peonin.
			Silk black-brown	Scarlet.
			Silk scarlet. HNO_2 slowly colours it yellow	Red Woods.
	Silk decolourised	NaOH	Silk reddish-violet; HNO_3: Decolourises	Primrose.
			Silk reddish-violet; HNO_3: Silk becomes cream-coloured	Bengal Red.
			Silk grey	Murexide.

BLUE DYES—ON SILK.

HCl					Dye
No action	NaOH	Silk dirty green, the sodium hydroxide is coloured yellow			Indigo Carmine.
No action	NaOH	Silk at first dirty green, then loses colour. The alkaline solution gives a blue precipitate with HCl and ferric chloride			Prussian Blue.
No action	NaOH	Silk red, more or less of violet shade. On washing, it again turns blue	CaOCl₂: Silk de-colourised	HNO₃: Silk bluish-grey	Spirit Blue.
				HNO₃: Silk faint lilac	Alkali Blue.
				HNO₃: Silk Black-blue and then chestnut-brown	Water Blue.
				HNO₃: No action	Azo-Blue.
No action	NaOH	Shade changes to red, but by washing again becomes blue			Induline.
No action	No action	CaOCl₂	Silk slowly becomes grey. With HNO_3 reddish-grey		Basle Blue.
			No action. With HNO_3 silk becomes green, with HNO_3 a dirty green		Methylene Blue.
			Slowly decolourises. With HNO_3 silk green, then cream-coloured		Indigo.
Pale chestnut-brown. With water green, then greenish-blue					Indophenol.
Reddish-brown. With water blue					Alizarin Blue.
Scarlet. With water it turns first violet, then blue					Resorcin Blue.
Green. With water blue colour reappears instantly					Victoria Blue.

VIOLET DYES.

HCl	Dye
Blue, then bluish-grey and orange. Water again produces violet. NaOH reddens	Methyl Violet.
Blue. With water original colour reappears. With NaOH blue	Mauvein.
Reddish-brown	Gallein.

GREEN DYES.

HCl		Dye
No action. Fibre contains Fe_2O_3		Resorcin Green.
Silk grey, HCl coloured red-brown. On washing grey colour remains		Cœrulein.
Silk yellow. NaOH	Decolourises. Silk remains unchanged on heating to 100°	Malachite Green.
	Decolourises. On heating to 100° silk is coloured violet	Methyl Green.
Silk green-yellow. With NaOH brown-grey. On washing original colour does not reappear		Aldehyde Green.

IDENTIFICATION OF DYESTUFFS OR VEGETABLE FIBRES.

A scheme for this purpose by A. G. Green and his pupils, is reproduced for the greater part below.

Owing to the continuous production of new dyestuffs these are not, however, complete. For the identification of sulphide dyestuffs the test with stannous chloride is used, but it must be applied with due regard to the general properties of the dyes, as other substances, including many salt dyestuffs (sodium salts of sulphonic acids) are said to yield hydrogen sulphide under the same conditions.

Reagents.

Weak Ammonia.—1 c.c. ammonia (.880) to 100 c.c. of distilled water.

Dilute Sodium Hydroxide.—10 grm. sodium hydroxide in 100 c.c. water.

Saline Sodium Hydroxide.—10 c.c. sodium hydroxide solution (35 to 40% NaOH) to 100 c.c. saturated solution of common salt.

Formic Acid 90%.—Ordinary commercial strength.

Weak Formic Acid.—1 c.c. formic acid 90% to 100 c.c. distilled water.

Dilute Hydrochloric Acid.—5 c.c. hydrochloric acid (30%) to 100 c.c. of water.

Soap Solution.—10 grm. soap in 300 c.c. of water.

Tannin Solution.—10 grm. tannin and 10 grm. sodium acetate in 100 c.c. of water.

Bleaching Powder Solution.—Fresh solution at 50° Tw.

Hydrosulphite A (same as for wool).—10% solution of hydrosulphite NF or of hydralite, or a 5% solution of hydrosulphite NF conc., or of rongalite (formaldehyde compounds of hydrosulphurous or of sulphoxylic acids).

Hydrosulphite B (same as for wool).—The preceding slightly acidified by addition of 1 c.c. glacial acetic acid to 200 c.c. of solution.

Hydrosulphite X.—Dissolve 50 grm. of rongalite or hydrosulphite NF conc. in 125 c.c. of hot water. Grind 1 grm. of anthraquinone (precipitated not sublimed) to a fine powder, and reduce to a smooth paste with a little of the rongalite solution. Add this paste to the remaining solution hot, and heat the whole for 1 or 2 minutes at about

90°. Then dilute with cold water to 500 c.c. and after standing till cold add 1.5 c.c. of glacial acetic acid. Keep in a well stoppered bottle with greased stopper. The reagent should be tested occasionally by trying its effect on cotton dyed with α-Naphthylamine Bordeaux, which should be fully discharged after boiling for 1 or 2 minutes. The anthraquinone may be replaced by β-hydroxyanthraquinone, which can be employed in the same way or previously dissolved in a little alcohol before it is added to the hydrosulphite. It has the advantage of giving a clearer solution, but is not so generally available. The presence of the anthraquinone greatly increases the reducing power of this solution.

Persulphate Solution.—A cold saturated solution of potassium persulphate, or a 2% solution of ammonium persulphate.

Acid Stannous Chloride.—100 grm. stannous chloride to 100 c.c. hydrochloric acid (30%) and 50 c.c. water. In testing for sulphide colours this reagent may be replaced if desired by a strong solution of titanous chloride.

Procedure.

General.—All the tests are performed in test-tubes, usually with pieces of material about 0.5 in. to 0.75 in. square which are covered with from 1.5 to 2 in. of the reagent. The degree of stripping is judged by comparing the depth of shade remaining against that of the original pattern. The colour of the stripping solution is misleading, and can scarcely be relied upon as a guide. In testing the colours of calico prints the particular shades should be cut out and the reactions tried upon them separately. With cotton and wool or cotton and silk unions the weft is separated from the cotton warp and both submitted to examination. Doubt may exist as to how a particular shade should be classified, whether, for instance, a reddish-blue is to be regarded as a blue of a violet. In such cases the tables referring to both shades should be employed. The same remark applies to possible mixtures; thus in examining a certain green shade, both the yellow and the blue tables may require to be used. To distinguish between individual dyestuffs of the same group, the reactions toward concentrated sulphuric acid, sodium hydroxide, etc., may be employed, as published in the tables given in this book on pages 540 to 621, and those of Lange, Gnehm, Herrmann, and others. For additional confirmation it is well to compare the sample both as to shade and reactions with a dyed

pattern of the colouring matter or colouring matters to which it is believed to correspond.

In many instances the analytical procedure may be greatly simplified by exclusion of dyestuffs, the presence of which is rendered improbable or impossible by the special circumstances of the case, *e.g.*, by the fibre, shade, or mode of application of the colour.

Stripping Test for Acid Colours.—A few salt dyestuffs are partially stripped by weak ammonia, and may thus give rise to the impression that they are acid colours. To avoid this error it is advisable to add a small piece of white cotton when carrying out the test. If the dyestuff is an acid one, the cotton is either not tinted or becomes white on boiling a second time with weak ammonia.

Transference of Basic Colours to Wool.—The tannin mordant is first removed, as in testing for a basic colour, by boiling the pattern for half a minute with saline sodium hydroxide. It is then well washed to remove all alkali, and is boiled with a piece of white wool (half the size of the cotton or less) in a little plain water for 1 or 2 minutes. In most cases the dye base leaves the cotton almost entirely, and dyes the wool a full shade. If the colour does not develop on the wool 1 or 2 drops of weak formic acid (1 : 100) may be added. In the case of a few dyestuffs which are more difficult to strip (*e. g.*, basic greys), it is necessary to extract the colour with dilute hydrochloric acid (1 : 20), carefully neutralising the extract with ammonia before adding the wool.

Transference of Acid Colours to Wool.—The cotton is boiled with a small piece of wool and weak formic acid (1 : 100).

Tannin Test for Basic Colours.—Add a few drops of tannin solution to the formic acid extract. Shake well, and if the precipitate does not form at once allow to stand a few minutes. Some colouring matters, such as the rhodamines, gallocyanines, and chrome colours of the rosaniline series (which contain carboxyl or hydroxyl groups in addition to basic groups) only precipitate slowly, while the precipitate, being more finely divided, is sometimes difficult to see.

Bleeding Test for Salt Dyestuffs.—In testing for salt dyestuffs by the bleeding test, the sample is placed in a test-tube together with a smaller piece of white mercerised cotton cloth and boiled with 1% soap solution for about a minute. The soap solution may also be replaced by a 5% solution of sodium carbonate.

Lead Acetate Test for Sulphide Colours.—The sample is just

covered with acid stannous chloride solution. The mouth of the test-tube is closed by a cap of filter-paper closely wrapped round it, into the centre of which is placed, by means of a glass rod, one drop of lead acetate solution. The contents of the test-tube are slowly heated to the boiling-point when a blackish-brown stain of lead sulphide appears if a sulphide colour is present. The brown spot will again disappear on boiling the solution longer, owing to the decomposition of the lead sulphide by the hydrochloric acid evolved. In order to avoid the possibility of error through extraneous sulphur present on the cotton, the pattern may be previously boiled with 10% sodium hydroxide. It must, however, be borne in mind that the indications of the sulphide dyestuffs are rendered less sharp by this latter treatment. It is important to pay special attention to the cleanliness of the test-tubes employed for this test, as it is found that tubes which have been previously used for hydrosulphite reductions acquire a thin invisible deposit of sulphur upon their walls, which on boiling with stannous chloride gives rise to hydrogen sulphide and thus may lead to error.

Reduction and Reoxidation Tests.—The reduction with hydrosulphite X is carried out by boiling the sample with the reagent for from 0.5 to 2 minutes. The azines, thiazines, oxazines, etc., and most of the azo dyestuffs are fully reduced in about half a minute, but the insoluble azo colours and some salt dyestuffs require from 1 to 2 minutes to complete their reduction. In testing the reoxidisability by air, the reduced sample should be exposed to the fumes from an ammonia bottle, which in many cases accelerate oxidation.

TABLE I.—YELLOW AND ORANGE COLOURS.

<table>
<tr><td colspan="10">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td colspan="3">The colour is stripped. Boil with acidified water and small piece of white wool.</td><td colspan="7">The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse and boil twice with weak formic acid (1 : 100).</td></tr>
<tr><td rowspan="4">Colour not transferred to the wool. Sn is present in ash.</td><td colspan="2" rowspan="2">Colour is transferred to the wool: Acid dyestuff. Boil wool with hydrosulphite B.</td><td colspan="4">The colour is completely destroyed, both alkaline and acid solutions and the fibre being colourless. Treat original fibre with cold ammonium sulphide.</td><td colspan="3">The colour is completely or largely stripped, giving a coloured acid extract which is precipitated by tannin solution: Basic dyestuff. Transfer to wool and boil with hydrosulphite B.</td></tr>
<tr><td rowspan="3">Fibre blackened. Cr present in ash.</td><td colspan="3">Fibre is not blackened. Boil with hydrosulphite X.</td><td colspan="2">Wool is not decolourised. Boil cotton with hydrochloric acid (1 : 20).</td><td rowspan="3">Wool is permanently decolourised: Azo group.</td></tr>
<tr><td rowspan="2">Not decolourised: Pyrone or quinoline group.</td><td rowspan="2">Permanently decolourised: Azo group.</td><td colspan="2">Not decolourised. Test for Al in ash.</td><td rowspan="2">De-colourised.</td><td rowspan="2">De-colourised.</td><td rowspan="2">Not decolourised. The conc. H_2SO_4 and alcoholic solutions are fluorescent: Acridine group.</td></tr>
<tr><td>Al present.</td><td>Al absent.</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td></tr>
<tr><td>Persian berries on tin mordant.</td><td>Quinoline Yellow, Eosin Orange.</td><td>Indian Yellow, Orange IV, G, etc.</td><td>Chrome Yellow or Chrome Orange (lead chromate).</td><td>Alizarin Yellow A.</td><td>Thioflavine T.</td><td>Flavinduline</td><td>Auramine.</td><td>Phosphine, Benzoflavine, Acridine Yellow, Acridine Orange, etc.</td><td>Chrysoidine, Tannin Orange, Janus Yellow, etc.</td></tr>
</table>

1. Brilliant yellow is largely stripped by weak ammonia, but if white cotton is present it will be stained.
2. Sulphide yellows of the thiazol class, such as Katigene yellow 2G, pyrogene yellow, etc., stain white cotton slightly when boiled in soap.
3. Diamond flavine, if not fully fixed, may stain cotton from a soap solution.

TABLE I.—YELLOW AND ORANGE COLOURS.—*Continued.*

<table>
<tr><td colspan="10">Boil with weak ammonia (1:100).</td></tr>
<tr><td colspan="10">The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse and boil twice with weak formic acid (1:100).</td></tr>
<tr><td colspan="10">The colour is not stripped or the acid extract is not precipitated by Tannin solution. Reduced with Hydrosulphite X.</td></tr>
<tr><td colspan="4">Decolourised and colour not restored by air or persulphate: Azo dyestuff (including stilbene group). Boil with soap solution and white mercerised cotton.</td><td colspan="6">The colour is unaffected or changed in shade (becoming yellower, browner, or blue). Apply lead acetate test.</td></tr>
<tr><td colspan="2" rowspan="2">White cotton is stained: Salt colour. Test ash for Cr and Cu.</td><td colspan="2" rowspan="2">White cotton is not stained. Boil with pyridine.</td><td rowspan="3">H_2S is evolved. After reduction with hydrosulphite the original colour is rapidly restored by air: Sulphide dyestuff.</td><td colspan="5">No H_2S is evolved. Boil with soap solution and white mercerised cotton.</td></tr>
<tr><td colspan="2">The white cotton is stained:— Thiazole salt dyestuff.</td><td colspan="3">The white cotton is not stained: Mordant or vat dyestuff.</td></tr>
<tr><td>Cr and Cu absent: Salt azo dyestuff untreated.</td><td>Cr or Cu present: Salt azo dyestuff "after-treated."</td><td>Colour is stripped: Insoluble azo colour.</td><td>Colour is not stripped. Cr present in ash: Azo mordant colour.</td><td>The colour after reduct'n with hydrosulphite can be diazotised and developed red with betanaphthol.</td><td>The colour after reduction cannot be diazotised and developed.</td><td>The reduced colour is yellow or brownish-yellow. Al or Cr in ash.</td><td>The reduced colour is brown, restored to orange by persulphate.</td><td>The reduced colour is blue, restored to yellow on exposure to air.</td></tr>
<tr><td>11
Chrysophenin, Chrysamin, Tolylene Yellow and Orange, Stilbene Yellows and Oranges, Benzo, Congo, Diamine, and Dianil Yellows and Oranges, Pyramine Orange, etc.</td><td>12
The preceding coppered or chromed.</td><td>13
Metanitraniline Orange or Nitrotoluidine Orange (formed on fibre).</td><td>14
Chrome Orange, Alizarin Yellow R, GG, etc., diamond flavine, flavazol, etc.</td><td>15
Immedial, Katigene, Pyrogene, Thiogene, Sulphur, etc., Yellows and Oranges.</td><td>16
Primuline developed with phenol or with resorcinol. Cotton Yellow G and R, Oriol Yellow, Dianil Yellow, etc.</td><td>17
Chlorophenine, Chloramine Yellow, Diamine Fast Yellow B, FF, and C, Clayton Yellow, Thiazol Yellow, Thioflavine S, etc. Primuline developed with hypochlorite.</td><td>18
Persian berries on Al or Cr mordants.</td><td>19
Alizarin Orange on Al mordant.</td><td>20
Flavanthrene.</td></tr>
</table>

TABLE II.—RED COLOURS.

Boil with weak ammonia (1 : 100).					
The colour is stripped: **Acid dyestuff.** Transfer to wool and boil with hydrosulphite B.		The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice for 1 minute with weak formic acid (1 : 100).			
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic dyestuff** (on tannin or other mordant). Transfer to wool and boil with hydrosulphite A.			
Not decolourised: **Pyrone group.**	Decolourised. Colour not restored by air or persulphate: **Azo group.**	Wool not decolourised: **Pyrone group.**	Wool decolourised. Colour returns on exposure to air: **Azine group.**	Wool decolourised. Colour does not return on exposure to air but is restored by persulphate: **Triphenylmethane group.**	Wool decolourised. Colour not restored by air or by persulphate: **Azo group.**
1	2	3	4	5	6
Eosins, Phloxin, Erythrosin, Rose Bengal, etc.	Crocein Scarlets, Briliant Croceines, Fast Reds, etc.	Rhodamines, Rhodines, Irisamine, Acridine Reds, etc.	Safranines, Rhoduline Reds and Pink, Azine Scarlet, Induline Scarlet, Neutral Red, etc.	Magenta, Fuchsine, Isorubine, Cerise, Grenadine, etc.	Janus Red.

Janus Claret Red does not transfer to wool very easily.

TABLE II.—RED COLOURS.—*Continued.*

Boil with weak ammonia (1 : 100).								
The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice for 1 minute with weak formic acid (1 : 100).								
The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X.								
Decolourised and colour not restored by air or by persulphate: **Azo group.** Boil with soap solution and white mercerised cotton.				Decolourised. Colour returns on exposure to air: **Azine** or **indigo group.** Apply lead acetate test.		Colour change to greenish-yellow which can be diazotised and developed red with betanaphthol: **Primuline azo colour.**	Colour unaffected or changed in shade (becomes browner, etc.): **Anthracene group.** Boil with 90% formic acid.	
The white cotton is stained: **Salt dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with pyridine.						
No Cr or Cu present: **Azo salt dyestuff.**	Cr or Cu present: **Azo salt dyestuff after treated.**	The colour is stripped: **Insoluble azo colour.**	The colour is not stripped. Cr in ash: **Mordant azo dyestuff.**	H_2S is evolved: **Sulphide dyestuff.**	No H_2S evolved. Red vapours formed on heating fibre in dry test-tube.		Colour is stripped. Test ash for mordant.	Colour not much unaffected. Test ash for Cr.
							Al present.	Cr present.
7	8	9	10	11	12	13	14	15
Benzopurpurine, Diamine Scarlets, Diamine Reds, Benzo Fast Scarlets, Diazo Brilliant Scarlet, Rosanthrenes, Sambesi Red, Erica, Diamine Rose, Geranine, Rosophenine, etc.	Diamine Fast Red F, etc.	Paranitraniline Red, Alphanaphthylamine Bordeaux, Chloranisidine Pink, Nitroanisidine Pink.	Chrome Red, Brilliant Chrome Red, Chrome Bordeaux, etc.	Thiogene Rubine, etc.	Thioindigo Red, Thioindigo Scarlet.	Primuline developed with betanaphthol or with R-salt.	Turkey Red, Alizarin Red, Alizarin Pink, Alizarin Maroon.	Alizarin, Purpurins or Alizarin Maroon on Cr mordant.

TABLE III.—PURPLE AND VIOLET COLOURS.

<table>
<tr><td colspan="8">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td colspan="2" rowspan="3">The colour is stripped: Acid dyestuff. The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate: Triphenylmethane group.</td><td colspan="6">The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice for 1 minute with weak formic acid (1 : 100).</td></tr>
<tr><td colspan="6">The colour is completely or largely stripped giving a coloured acid extract, which is precipitated by tannin solution: Basic dyestuff (on tannin or other mordant) or basic mordant dyestuff. Boil with saline sodium hydroxide, rinse well, and boil with small piece of white wool and plain water.</td></tr>
<tr><td colspan="4">The wool is dyed: Basic dyestuff. Boil wool with hydrosulphite A.</td><td colspan="2">The wool is not dyed. Cr is present in ash: Basic mordant dyestuff. Boil cotton with hydrosulphite X.</td></tr>
<tr><td>The ammoniacal solution is colourless, but becomes blue on acidifying.</td><td>The ammoniacal solution is violet.</td><td>Not decolourised: Pyrone group.</td><td>Decolourised. Colour returns on exposure to air: Azine (oxazine or thiazine) group.</td><td>Decolourised. Colour does not return in air, but is restored by persulphate: Triphenylmethane group.</td><td>Decolourised. Colour is not restored by air or persulphate: Azo group.</td><td>Decolourised. Colour returns on exposure to air: Oxazine group.</td><td>Decolourised only slowly. Colour does not return in air, but is restored by persulphate: Triphenylmethane group.</td></tr>
<tr><td>1
Red shades of Soluble and Alkali Blues.</td><td>2
Acid Violets, Formyl Violets, etc.</td><td>3
Anisolin.</td><td>4
Methylene Violet, Rhoduline Violet, Iris Violet, Neutral Violet, Tannin Heliotrope, etc.</td><td>5
Methyl Violets, Ethyl Violet, Benzyl Violet, Crystal Violet, etc.</td><td>6
Janus Claret Red, etc.</td><td>7
Gallocyanin, Gallamine Blue, Prune, etc.</td><td>8
Chrome Violet.</td></tr>
</table>

TABLE III.—PURPLE AND VIOLET COLOURS.—*Continued.*

<table>
<tr><td colspan="11">Boil with **weak ammonia** (1:100).</td></tr>
<tr><td colspan="11">The colour is not stripped. Boil for **half minute** with **saline sodium hydroxide**, rinse, and boil twice for 1 minute with **weak formic acid** (1:100).</td></tr>
<tr><td colspan="11">The colour is not stripped or the acid extract is not precipitated by **tannin** solution. Reduce with hydrosulphite X.[1]</td></tr>
<tr><td colspan="5">Decolourised and colour not restored by air or persulphate: Azo group or alizarin on iron (decolourised slowly). Boil with soap solution and white mercerised cotton.</td><td colspan="2" rowspan="2">Decolourised. Colour is restored on exposure to air: Azine, oxazine, or thiazine group. Apply lead acetate test.</td><td colspan="4">The colour is unaffected or changed in shade: Pyrone or anthracene group (also one or two sulphide dyestuffs).</td></tr>
<tr><td colspan="2">The white cotton is stained: Salt dyestuff. Test ash for Cr and Cu.</td><td colspan="3">The white cotton is not stained. Boil with hydrochloric acid (1:20).</td><td rowspan="3">The colour is unaffected. Al or Cr present in ash: Pyrone or anthracene mordant colour.</td><td colspan="3">The colour is changed to brown. Apply lead acetate test.</td></tr>
<tr><td rowspan="2">No Cr or Cu present: Azo salt dyestuff.</td><td rowspan="2">Cr or Cu present: Azo salt dyestuff. after-treated.</td><td rowspan="2">Colour destroyed, giving yellow solution. Fe present in ash: Alizarine on Fe mordant.</td><td colspan="2">The colour is not stripped. Boil with pyridine.</td><td rowspan="2">H₂S is evolved: Sulphide dyestuff.</td><td rowspan="2">No H₂S is evolved. Cr is present in ash: Mordant oxazine dyestuff (not falling in Group 7).</td><td rowspan="2">H₂S is evolved: Sulphide dyestuff.</td><td colspan="2">No H₂S is evolved. Test ash for Al and Cr.</td></tr>
<tr><td>The colour is stripped: Insoluble azo color.</td><td>The colour is not stripped Cr present in ash: Mordant azo dyestuff.</td><td>Al or Cr present: Anthracene mordant dyestuff.</td><td>Al and Cr absent. Anthracene vat dyestuff.</td></tr>
<tr><td>9</td><td>10</td><td>11</td><td>12</td><td>13</td><td>14</td><td>15</td><td>16</td><td>17</td><td>18</td><td>19</td></tr>
<tr><td>Violets of the Diamine, Benzo, Congo, Hessian, Columbia, Chlorazol, Chlorantine, Dianil, Oxamine, and Rosanthrene series.</td><td>The preceding coppered or chromed.</td><td>Alizarin Purple.</td><td>Benzidine Puce.</td><td>Chrome Bordeaux, Chrome Prune, etc.</td><td>Thiogene Violet, Katigene Violet, etc.</td><td>Gallamine Blue, Gallocyanine. etc.</td><td>Gallein, Alizarin Violet, Alizarin Claret, Alizarin Cyclamine, Alizarin on Cr mordant.</td><td>Thiogene Dark Red, etc.</td><td>Alizarin Cyanine 3R, Alizarin Bordeaux.</td><td>Violanthrene</td></tr>
</table>

[1] Alizarin on chromium becomes rather browner on reduction with hydrosulphite X.

TABLE IV.—BLUE COLOURS.

Boil with weak ammonia (1 : 100).						
The colour is stripped: **Acid dyestuff** (or Prussian blue).[1]		The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice with weak formic acid (1 : 100).				
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic dyestuff** (on tannin or other mordant) or **basic mordant dyestuff.** Boil with saline sodium hydroxide, rinse well, and boil with small piece of white wool and plain water.				
The extract is colourless, but becomes blue on acidification. Transferred to wool, the blue is decolourised by hydrosulphite A, and restored by persulphate: **Triphenylmethane group.**	The extract is colourless and remains so on acidification. $FeCl_3$ gives a blue precipitate.	The wool is dyed: **Basic dyestuff.** Boil wool with hydrosulphite A.			The wool is not dyed. Cr present in ash: **Basic mordant dyestuff.** Boil cotton with hydrosulphite X.	
		Decolourised. Colour returns on exposure to air: **Azine, oxazine, or thiazine group.**	Colour changes to red just before being decolourised. Colour returns violet or blue: **Safranine azo dyestuff.**	Decolourised. Colour does not return on exposure to air, but is restored by persulphate: **Triphenylmethane group.**	Decolourised. Colour returns on exposure to air: **Oxazine group.**	Decolourised slowly. Colour restored only by persulphate: **Triphenylmethane group.**
1	2	3	4	5	6	7
Alkali or Soluble Blues.	Prussian Blue.	Methylene Blue, New Methylene Blue, Nile Blue, Capri Blue, Indazine, Basle Blue, Metaphenylene Blue, Meldola's Blue, Fast Blue, Cresyl Blue, Rhoduline Blue, Nitroso Blue, etc.	Indoïne Blue, Janus Blue, Naphthindone Blue, Diazine Blue, etc.	Victoria Blue, Night Blue, Turquoise Blue, Setocyanine, etc.	Gallocyanine, Celestine Blue, Prune, etc.	Chrome Blue.

[1]Alkali blue dyed on a tannin and tin mordant is only partly stripped by weak ammonia, the solution being colourless.

TABLE IV.—BLUE COLOURS.—*Continued.*

<table>
<tr><td colspan="11">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td colspan="11">The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice with weak formic acid (1 : 100).</td></tr>
<tr><td colspan="11">The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X.</td></tr>
<tr><td colspan="3">Decolourised and colour not restored by air or persulphate: Azo group.
Boil with soap solution and white mercerised cotton.</td><td colspan="3">Decolourised. Colour is restored on exposure to air:
Azine, oxazine, thiazine or indigo group. Apply lead acetate test.</td><td rowspan="3">Colour changed to greenish-yellow, which can be diazotised and developed red with betanaphthol: Primuline azo colour.</td><td colspan="4">Colour unaffected or changed in shade (becoming darker, browner, etc.):
Anthracene mordant or anthracene vat dyestuff (also ultramarine). Boil with 90% formic acid.</td></tr>
<tr><td colspan="2">The white cotton is stained: Salt dyestuff.
Test ash for Cr and Cu.</td><td rowspan="2">The white cotton is not stained. Colour is stripped by boiling pyridine: Insoluble azo colour.</td><td rowspan="2">H_2S is evolved: Sulphide dyestuff.</td><td colspan="2">No H_2S is evolved: Heat fibre carefully in dry test-tube.</td><td colspan="2">The colour is stripped. Al in ash. Apply lead acetate test.</td><td colspan="2">The colour is not much affected. Test ash for Cr.</td></tr>
<tr><td>No Cr or Cu present: Azo salt dyestuff.</td><td>Cr or Cu present: Azo salt dyestuff after-treated.</td><td>Violet vapours evolved.</td><td>No coloured vapour. Cr in ash: Mordant thiazine or oxazine (not falling in Group 6).</td><td>H_2S evolved.</td><td>No H_2S evolved: Alizarine dyestuff on Al.</td><td>Cr present in ash: Alizarine dyestuff on Cr.</td><td>Cr absent: Anthracene vat dyestuff.</td></tr>
<tr><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td><td>13</td><td>14</td><td>15</td><td>16</td><td>17</td><td>18</td></tr>
<tr><td>Blues of the Diamine, Benzo, Congo, Columbia, Chlorazol, Dianil, Oxamine, Chicago etc., series.</td><td>The preceding coppered or chromed.</td><td>Dianisidine Blue.</td><td>Blues of the immedial, katigene, thiogene, pyrogene, sulphur, etc., series.</td><td>Indigo.</td><td>Brilliant Alizarin Blue, Delphine Blue, Gallophenine, etc.</td><td>Primuline developed with naphthylamine ether.</td><td>Ultramarine.</td><td>Alizarin Cyanines or Anthracene Blues on Al mordant.</td><td>Alizarin Blue, Alizarin Cyanines or Anthracene Blues on Cr mordant.</td><td>Indanthrene, Cyananthrene.</td></tr>
</table>

TABLE V.—GREEN COLOURS.

<table>
<tr><td colspan="9">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td rowspan="5">The colour is stripped: Acid dyestuff. The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate: Triphenylmethane group.</td><td colspan="8">The colour is not stripped, Boil for half minute with saline sodium hydroxide, rinse and boil twice with weak formic acid.</td></tr>
<tr><td colspan="4" rowspan="2">The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: Basic dyestuff (on tannin or other mordant) or basic mordant dyestuff. Boil with saline sodium hydroxide, rinse well, and boil with white wool and plain water.</td><td colspan="4">The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X.</td></tr>
<tr><td colspan="4">Decolourised and colour not restored by air or persulphate: Azo or nitroso group. Boil with soap solution and white mercerised cotton.</td></tr>
<tr><td colspan="3">The wool is dyed: Basic dyestuff. Boil wool with hydrosulphite A.</td><td rowspan="2">The wool is not dyed. Cr in ash. Cotton decolourised by hydrosulphite X, the colour not returning in air but restored by persulphate: Triphenylmethane group.</td><td colspan="2">The white cotton is stained: Salt dyestuff. Test ash for Cr and Cu.</td><td colspan="2">The white cotton is not stained. Boil with hydrochloric acid (1 : 20).</td></tr>
<tr><td>Decolourised. Colour returns on exposure to air: Azine, oxazine, or thiazine group.</td><td>Colour becomes red just before being decolourised. Colour returns violet or green on exposure to air: Safranine azo group.</td><td>Decolourised. Colour does not return on exposure to air, but is restored by persulphate: Triphenylmethane group.</td><td>Cr and Cu absent: Azo salt dyestuff.</td><td>Cr or Cu present: Azo salt dyestuff. after-treated.</td><td>Colour destroyed. Fe is present in the ash: Nitroso group.[1]</td><td>Not decolourised. Cr is present in the ash: Mordant azo dyestuff.</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td></tr>
<tr><td>Acid Greens.</td><td>Fast Green M, Methylene Green, Azine Green, Capri Green, etc.</td><td>Janus Green, Diazine Green, etc.</td><td>Brilliant Green, Malachite Green, Methyl Green, Victoria Green, Seto-Glaucine, etc.</td><td>Chrome Green.</td><td>Diamine Green, Benzo Green, Columbia Green, Chloramine Green, etc.</td><td>The preceding coppered or chromed.</td><td>Russian Green, Fast Green O, Steam Green, Alsace Green, Gambines, Dioxin, etc.</td><td>Diamond Green, etc.</td></tr>
</table>

[1] Greens of the nitroso group (Gambins, etc.) may become black on reduction if the hydrosulphite X is insufficiently acid (formation of FeS).

TABLE V.—GREEN COLOURS.—*Continued.*

Boil with weak ammonia (1 : 100).									
The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse and boil twice with weak formic acid.									
The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X.									
Decolourised. Colour returns on exposure to air: **Azine, oxazine, or thiazine group.** Apply lead acetate test.		The colour is unaffected or changed to red, brown, blue, etc. Test ash for Cr and Ni.							
		The colour is changed to greenish-yellow, which can be diazotised and developed red with betanaphthol: **Primuline azo group.**	The ash contains Cr or Ni: **Anthracene mordant dyestuff.**				No Cr or Ni present in ash: **Anthracene vat dyestuff.**		
			Reduced colour is brownish-red. Green restored by persulphate but not by air. Boiling HCl (1 : 20) gives bright green solution.	Reduced colour is brown. Green shade returns on exposure to air. Boil with hydrochloric acid (1 : 20).					
H₂S is evolved: **Sulphide dyestuff.**	No H_2S is evolved: **Mordant oxazine** (or **thiazine**).			Colour unaffected. Solution colourless. Cr in ash.	Colour of fibre becomes grey, solution red. Ni in ash.	Colour of fibre rather paler, solution brownish-yellow.	Reduced colour is brownish-olive. H_2S evolved on applying lead acetate test.	Reduced colour is dark maroon. Green shade restored by air.	Reduced colour is blue. Green shade restored by air.
10	11	12	13	14	15	16	17	18	19
Greens of the Immedial, katigene, thiogene, pyrogene, sulphur, and thionol series.	Gallanilic Green, Indalizarin, etc.	Primuline developed with aminodiphenylamine.	Alizarin Viridine, Brilliant alizarin Viridine.	Alizarin Green S on Cr mordant.	Alizarin Green S on Ni Mg mordant.	Cœrulein. Anthracene Green.	Olivanthrene.	Viridanthrene.	Algole green, Indanthrene in admixture with flavanthrene.

TABLE VI.—BROWN COLOURS.

<table>
<tr><td colspan="8">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td rowspan="5">The colour is stripped:
Acid dyestuff.
Transferred to wool it is permanently decolourised by hydrosulphite A:
Azo group.</td><td colspan="7">The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice with weak formic acid (1 : 100).</td></tr>
<tr><td rowspan="4">The colour is stripped giving acid extract which is precipitated by tannin solution:
Basic dyestuff.
The dyestuff transferred to wool is permanently decolourised by hydrosulphite A:
Azo group.</td><td colspan="6">The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X.</td></tr>
<tr><td colspan="6">Decolourised and colour not restored on exposure to air or by persulphate:[1]
Azo group and **mineral colours.** Boil with soap solution and **white** mercerised cotton.</td></tr>
<tr><td colspan="2" rowspan="2">The white cotton is stained:
Salt dyestuff.
Test ash for Cr and Cu.</td><td colspan="4">The white cotton is not stained. Boil with pyridine.</td></tr>
<tr><td colspan="2">The colour is stripped:
Insoluble azo colour.
Test ash for Cu.</td><td colspan="2">The colour is not stripped:
Mineral colour.
Treat with sodium bisulphite in the cold.</td></tr>
<tr><td></td><td></td><td>Cr and Cu absent:
Azo salt dyestuff.</td><td>Cr or Cu present:
Azo salt dyestuff. aftertreated.</td><td>Cu absent.</td><td>Cu present.</td><td>Decolourised.</td><td>Not decolourised.</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td></tr>
<tr><td>Fast Brown, Naphthylamine Brown, Acid Brown, etc.</td><td>Bismarck Brown, Janus Brown, etc.</td><td>Browns of the diamine, benzo, Congo, dianil, Columbia, Hessian, oxamine and toluylene series.</td><td>The preceding coppered or chromed.</td><td>Para Brown (Chrysoidine and paranitraniline), Benzidine or Tolidine Brown.</td><td>Paranitraniline Cutch (Para Red coppered).</td><td>Manganese bronze.</td><td>Iron buff, khaki (oxides of Cr and Fe).</td></tr>
</table>

[1] Iron buff and khaki may become black on reduction if the hydrosulphite X is insufficiently acid (formation of FeS).

TABLE VI.—BROWN COLOURS.—*Continued.*

Boil with weak ammonia (1 : 100).					
The colour is not stripped. Boil for half minute with saline sodium hydroxide, rinse, and boil twice with weak formic acid (1 : 100).					
The colour is not stripped or the acid extract is not percipitated by tannin solution. Reduce with hydrosulphite X.					
The shade is changed to greenish-yellow which can be diazotised and developed red with betanaphthol: **Primuline Azo colour.**	Unaltered or changed in shade, becoming darker, paler, yellower, etc. Apply lead acetate test.				
	H₂S is evolved: **Sulphide dyestuff.**	No H_2S is evolved. Test ash for Cr and Cu.			
		Cr or Cu (or both) present: **Mordant dyestuff.** Boil with HCl (1 : 20).			Cr and Cu absent: **Anthracene vat dyestuff, etc.**
		Completely stripped.	Not stripped or only slightly. Boil with dilute sodium hydroxide 10%.		
			Fibre and solution dull violet.	Solution brown, fibre unaffected.	
9	10	11	12	13	14
Primuline developed with metaphenylene diamine. Terra-cotta, etc.	Immedial cutch, Cross Dye Brown, Katigene Browns, Pyrogene Browns, Thiogene Browns. etc.	Anthragallol, Anthracene Brown, Alizarin Brown.	Alizarin Orange on Cr mordant, Alizarin or Purpurin on Cr.	Cutch.	Fuscanthrene, Paramine Brown (*p*-phenylene diamine oxidised on fibre).

TABLE VII.—BLACK AND GREY COLOURS.

Boil with weak ammonia (1 : 100).					
The colour is stripped: Acid dyestuff. The dyestuff transferred to wool and boiled with hydrosulphite A is permanently decolourised: **Azo group.**	The colour is not stripped. Boil with dilute hydrochloric acid (1 : 5).				
	The colour is stripped.			The colour is not stripped (or only slightly). Boil for 1 minute with saline sodium hydroxide, rinse, and boil withdilute hydrochloric acid (1 : 20).	
				The colour is largely stripped and the acid extract is precipitated by tannin solution: Basic dyestuff. Transfer to wool (see note) and boil with hydrosulphite A.	
	Fibre and solution colourless.	Solution orange. Fe in ash.	Solution red. Cr in ash.	Decolourised. Colour returns on exposure to air: **Azine, oxazine,** or **thiazine group.**	Colour becomes red just before being decolourised. Violet or violet-blue colour returns in air: **Safranine azo group.**
1	2	3	4	5	6
Naphthol Blacks, Naphthylamine Blacks, Palatine Black, etc.	Tannate of iron.	Logwood black on iron mordant.	Logwood black on chrome mordant, Noir Reduit.	Methylene Grey, New Methylene Grey, New Fast Grey, Nigrosine, etc.	Janus Black, Janus Grey, Diazine Grey.

Chrome black (By) becomes light brown on reduction with hydrosulphite X, and persulphates change the colour to dark brown but not to black.

TABLE VII.—BLACK AND GREY COLOURS.—*Continued.*

<table>
<tr><td colspan="8">Boil with weak ammonia (1 : 100).</td></tr>
<tr><td colspan="8">The colour is not stripped. Boil with dilute hydrochloric acid (1 : 5).</td></tr>
<tr><td colspan="8">The colour is not stripped (or only slightly). Boil for 1 minute with saline sodium hydroxide, rinse, and boil with dilute hydrochloric acid (1 : 20).</td></tr>
<tr><td colspan="8">The colour is not stripped or acid extract is not precipitated by tannin solution. Reduce with dyhrosulphite X.</td></tr>
<tr><td colspan="3" rowspan="2">Decolourised and colour not restored by air or persulphate: Azo group.
Boil with soap solution and white mercerised cotton.</td><td colspan="5">The colour is unaffected or changed in shade (becoming brown, maroon, etc.).</td></tr>
<tr><td colspan="2">The reduced colour is brown but is rapidly restored to black on exposure to air: Azine, oxazine, or thiazine group. Apply lead acetate test.</td><td rowspan="3">The reduced colour is brown. Only slowly and imperfectly restored to black by air but at once by persulphate. Cr present in ash: Naphthalene mordant dyestuff.</td><td colspan="2" rowspan="2">Colour not changed by reduction (or very slightly): Anthracene group. Test ash for Cr.</td></tr>
<tr><td colspan="2">The white cotton is stained. Test ash for Cr and Cu.</td><td rowspan="2">The white cotton is not stained. Colour is stripped by boiling pyridine: Insoluble azo colour.</td><td rowspan="2">H_2S is evolved. Fibre becomes colourless or pale buff on boiling with bleaching powder solution (5° Tw.). Sulphide dyestuff.</td><td rowspan="2">No H_2S is evolved. Fibre becomes reddish-brown on boiling with bleaching powder solution (5° Tw.). An oxidation black.</td></tr>
<tr><td>Cr and Cu absent: Azo salt dyestuff.</td><td>Cr or Cu present: Azo salt dyestuff. aftertreated.</td><td>Cr present: Anthracene mordant dyestuff.</td><td>Cr absent: Anthracene vat dyestuff.</td></tr>
<tr><td>7
Blacks of the diamine, oxydiamine, benzo, Columbia, dianil, Pluto, etc., series, also Diaminogen, Diazo Blacks etc., (developed or coupled).</td><td>8
The preceding coppered or chromed.</td><td>9
Azophor Black, etc.</td><td>10
Blacks of the immedial, katigene, cross dye, pyrogene, thiogene, thionol, pyrol, sulphur, etc., series.</td><td>11
Aged Aniline Black, Prussiate Black, one Bath Aniline Black, Steam Aniline Black, Diphenyl Black.</td><td>12
Naphthazarin S, Alizarin Black S, Alizarin Blue black SW, Naphthomelane.</td><td>13
Alizarin Cyanine Black, Alizarin Blue-black B.</td><td>14
Melanthrene.</td></tr>
</table>

Vat Dyes.—On account of their increasing importance the reactions of these dyes are given here in detail in the following tables.

The so-called Helindone or derived indigo colours give extremely fast shades. When their presence is suspected the following tests (Buckley, *J. Soc. D. and Col.*, 1910, **26**, 58) will help to identify them. On account of their high price they will be chiefly found on fancy materials which have to stand bleaching and severe washing:

TABLE SHOWING THE ACTION OF TITANOUS CHLORIDE AND CHLOROFORM ON THESE COLOURS.

Colour	$TiCl_3$ 1 : 5.	Chloroform
Indigo MLB/4B	Fibre olive-green	Intense blue solution.
Indigo MLB/5B	Fibre olive-green	Intense blue solution.
Indigo MLB/6B	Fibre green	Intense blue solution.
Helindone Orange R	Colour stripped to a thin dull orange.	Slightly sol., salmon pink solution.
Helindone Yellow 3GN	Colour becomes much lighter.	Insoluble.
Helindone Brown G	Fibre straw coloured	Very slightly soluble, solution has yellow tinge.
Helindone Red 3B	Fibre dull blue-violet	Red-violet solution.
Helindone Red B	Fibre dull red-violet	Very soluble, solution red and somewhat fluorescent.
Helindone Scarlet 8	Olive green	Very soluble, solution orange coloured.
Helindone Fast Scarlet R	Reddish-brown	Very soluble, solution red.

The vat dyes are all members of 3 classes.

(a) The anthracene class. These require in their application a strongly alkaline bath and are, therefore, confined to cotton dyeing; (b) the indigoid class which are applicable for both wool and cotton and (c) the recently introduced indocarbon-group which have not yet been examined. These, like indigo itself, can be sublimed from the fibre forming coloured vapours. Green and Frank (*J. S. D. and C.*, 1910, **26**, 83) propose the following scheme for the general identification of these dyes of the (a) and (b) classes.

1. Boil the fibre for about a minute with "hydrosulphite X." The indigoid dyestuffs are reduced to colourless or pale yellow leuco compounds from which the original colours are slowly regenerated upon exposure to air. In the case of certain red members of the indigoid class this reoxidation takes place in two stages, giving rise in the first instance to a different colour and finally to the original colour. This peculiarity is exhibited by Ciba Scarlet G, Algol Scarlet G, Helindone Scarlet S, and Ciba Bordeaux B. The anthracene deriva-

tives give deeply coloured reduction products which rapidly reoxidise to the original colour. These reduction products by reason of their characteristic shades may frequently serve as ameans of individual identification. The reagent termed "hydrosulphite X" is prepared in the manner described on page 516.

2. Heat a portion of the material in a dry test-tube and observe whether coloured vapours are produced, by looking down the length of the tube against a white background. The test requires some practice, as with light shades the indications are not always very distinct. The production of a coloured vapour indicates the presence of an indigoid dyestuff. However, two dyestuffs of this class, Ciba Green and Helindone Brown, although subliming in the solid state, fail to do so on the fibre.

I.—YELLOW AND ORANGE COLOURS.

	Commercial name	On reduction with hydrosulphite X the fibre becomes	The fibre heated in dry test-tube gives	With conc. sulphuric acid fibre becomes
Indigoids.....	Helindone Yellow 3G.	Light Greenish-yellow.	Yellow vapours.	Scarlet, with orange solution.
	Helindone Orange R.	Colourless	Orange vapours..	Bluish-violet, with violet solution.
Anthracenes ..	Indanthrene Yellow G and R.	Blue.............	No vapours......	Orange.
	Indanthrene Orange RT.	Browner.........	No vapours......	Orange-red.
	Indanthrene Golden Orange.	Unaltered.......	No vapours	Blue, with blue solution.
	Indanthrene Copper.	Orange..........	No vapours.....	Orange.
	Anthraflavone G.	Orange..........	No vapours.....	Maroon.
	Algole Yellow 3G.	Browner.........	No vapours.....	More intense yellow with yellow solution.
	Algole Yellow R.	Browner.........	No vapours.....	Light brown.
	Algole Orange R.	Browner.........	No vapours.....	First brown, then green.
	Cibanone Yellow R.	Orange-brown...	No vapours.....	Maroon.
	Cibanone-Orange R.	Brown..........	No vapours.....	Bordeaux.

II.—RED COLOURS.

	Commercial name	On reduction with hydrosulphite X the fibre becomes	The fibre heated in dry test-tube gives	With conc. sulphuric acid fibre becomes
Indigoids.....	Thioindigo Red B.	Light yellow, returning to red on exposure.	Red vapours....	Purple, quickly changing to green with green solution.
	Thioindigo Scarlet.	do.	Red vapours.....	Dark red-brown.
	Vat Red B.A.S. F./B.	do.	Red vapours....	Green, with green solution.
	Helindone Red B.	do.	Red vapours. ..	Dark green, with green solution.
	Helindone Red 3B	do.	Red vapours....	Dark green, with pale green solution.
	Helindone Scarlet S.	Light yellow, returning to brown and then to scarlet.	Orange red vapours.	Bright blue, with blue solution.
	Helindone Fast Scarlet R.	Light yellow, returning to scarlet on exposure.	Red vapours....	Dark blue, with bluish-violet solution.
	Ciba Red G......	Light yellow, returning to red on exposure.	Red vapours....	Dark reddish-brown.
	Ciba Scarlet G...	Light yellow, returning to maroon and then to scarlet.	Yellow vapours, giving red sublimate.	Bright green, with green solution.
	Ciba Bordeaux B.	Light greenish-yellow, returning to green, bluish-green, and then bordeaux.	Violet-red vapours.	Reddish-violet, with green solution.
	Algole Red 5G...	Light orange, returning to red.	Red vapours....	A deeper red.
	Algole Scarlet G.	Light yellow, returning to orange and then scarlet.	Yellow vapours, giving red sublimate.	Browner.
	Algole Pink R	Light yellow, returning to pink.	Red vapours....	Deeper red.
Anthracenes ..	Indanthrene Red.	Maroon.........	No vapours.....	Violet.
	Indanthrene Claret.	Brown..........	No vapours	Blue.
	Algole Red B....	Maroon.........	No vapours.....	Maroon.

III.—PURPLE AND VIOLET COLOURS.

Indigoids	Ciba Violet B and R.	Colourless	Violet vapours	Greenish-blue.
	Ciba Heliotrope	Colourless	Violet vapours	Bluish-violet.
	Algole Bordeaux	Light orange brown.	Reddish vapours.	Blue.
Anthracenes	Indanthrene Violet R extra.	Maroon	No vapours	Green.
	Indanthrene Violet RT.	Maroon	No vapours	Redder to maroon.

IV.—BLUE COLOURS.

	Commercial name	On reduction with hydrosulphite X the fibre becomes	The fibre heated in dry test-tube gives	With conc. sulphuric acid fibre becomes
Indigoids	Indigo	Pale yellow	Violet vapours	Olive green.
	Indigo MLB/2B, 4B, 5B, and 6B.	Pale yellow	Violet vapours	Slightly greener.
	Indigo MLB/T	Pale yellow	Violet vapours	Greener.
	Ciba Blue 2B	Pale yellow	Violet vapours	Greener.
	Bromindigo FB	Pale yellow	Violet vapours	Greener.
Anthracenes	Indanthrene Blue GC.	Darker and rather greener.	No vapours	Olive.
	Indanthrene Blue GCD.	Darker blue	No vapours	Olive.
	Indanthrene Blue RC.	Maroon	No vapours	Green.
	Indanthrene Dark Blue BO.	Reddish-brown	No vapours	Darker and greener.
	Algole Blue CF	Unchanged	No vapours	Light olive-brown.
	Algole Blue K	Darker, greenish-grey.	No vapours	Olive-brown.
	Algole Blue 3G	Darker and greener.	No vapours	Olive-green.

V.—GREEN COLOURS.

Indigoid.......	Ciba Green G....	Pale orange.....	No vapours	Blue, with blue solution.
Anthracenes ..	Indanthrene Green B.	Maroon.........	No vapours.....	Purple
	Indanthrene Olive.	Dark green......	No vapours.....	Dark brown.
	Algole Green B ..	Unchanged......	No vapours....	Slightly greener.
	Leucole Dark Green B.	Maroon.........	No vapours.....	Olive brown.

VI.—BROWN COLOURS.

Indigoid......	Helindone Brown G.	Yellow..........	No vapours.....	Bright bordeaux.
Anthracenes ...	Indanthrene Maroon.	Browner........	No vapours....	Light brown.
	Indanthrene Brown B.	Nearly black, or very dark maroon.	No vapours.....	Rather darker.
	Algole Brown B..	do.	No vapours.....	Darker.
	Leucole Brown B.	Maroon.........	No vapours.....	Unchanged.
	Cibanone Brown B.	Unchanged......	No vapours.....	Bluer.
	Cibanone Brown V.	Unchanged......	No vapours.....	Light brown.

VII.—GREY COLOURS.

Indigoids.....	Ciba Grey G....	Colourless......	Violet to bluish-grey vapours.	Greener, then orange-red.
	Ciba Grey B.....	Colourless.......	Violet to bluish-grey vapours.	Bluer, then orange-red.
Anthracene ...	Indanthrene Grey.	Rather redder grey.	No vapours.....	Brown.

Examination of Lakes.—No tables are available for the examination of lakes except those of Yerr. (*Coal Tar Colours in Aniline Lakes*, tr. by C. Mayer, London, 1910). These depend upon certain tests which include solubility in water, alcohol or acetic acid, reactions with sulphuric acid, sodium hydroxide, rate of colour change with acid stannous chloride, etc. Of late years many insoluble azo

dyes have been introduced as lakes and may be examined by the recognised methods for these dyes with more or less success. The inorganic constituents may be investigated by an examination of the ash after incineration. A treatment with strong acids or alkalies followed by the usual examination for dyes might sometimes lead to the detection of the actual dyes present. The composition of these lakes is in most cases not declared by the manufacturers. The alizarin lakes are of special value on account of their fastness to light. Those produced from basic colours on a tannic acid base if properly prepared are satisfactory in this respect in most cases.

In the case where these lakes are used as pigments an actual trial against a sample of known purity and colour is generally adopted in practice, the "covering power," fastness and such like properties being carefully noted.

General Reactions of Dyed Fabrics.

In the following tables of individual reactions which are abstracted from several sources, the individual reactions of many important dyes are given but, although this method of testing is generally advocated, it is not recommended to the analyst until the other methods already indicated are exhausted.

Various abbreviations are employed with the object of saving space, but they will probably be readily intelligible without special description.

The reagents applied are concentrated hydrochloric acid (sp. gr. 1.11), concentrated sulphuric acid, sodium hydroxide (10% solution), strong ammonia, a hydrochloric acid solution of stannous chloride, alcohol, and certain special reagents. The experiments are best made by treating portions of the fibre or fabric in small porcelain dishes, which can afterward be inclined so as to allow the liquid to drain to the side and permit the ready observation of any colour it may have acquired. In some cases, as when fluorescence it to be looked for, it is desirable to employ test-tubes instead of porcelain capsules. When nitric acid is employed, it should be applied to the fabric with a glass rod, when any change in the colour of the spot touched will be readily seen.

I. RED COLOURS.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Magenta	Yellow.	Yellow.	Brown-yellow.	Yellow.	Paler.	....
Acid Magenta	Paler.	Pink.	Paler.	Pink.	Decol.	....
Safranine	Blue.	Yellow.	Green.	Green.	....	Pink.
Magdala Red	No change.	....	No change.	....	No change.	
Eosin A	Yellow.	....	Yellow.	Yellow.	Yellow.	Pink fluorescence.
Methyl Eosin	Yellow.	....	Yellow.	Yellow.	Pink.	Pink fluor.
Phloxin	Yellow.	....	Yellow.	....	Pink.	Pink.
Erythrosin	Orange.	....	Yellow.	Orange.	Pink.	Pink.
Rhodamine	Red.	Colourless.	Red.	Colourless.	Bluer.	Colourless.
Aurin	Yellow.	Yellow.	Yellow.	....	....	Red.
Croceïn Scarlet 7 B	Violet.	Colourless.	Blue.	Blue.	Blue.	....
Biebrich Scarlet	Violet.	Colourless.	Green.	Green.	Violet.	Colourless.
Patent Fast Red	Darker.	Red.	Violet.	Colourless.	Paler.	Red.
Fast Ponceau B	Violet.	Colourless.	Green.	Green.	Violet.	Colourless.
Scarlet 2 R	Decol. hot.	Extracted hot.	No action, dilute.	Extracted conc.	Decol.	....
Scarlet 3 R	No change.	Red.	No action.	....	Decol.	Red.
Claret Red B	No change.	Violet.	Blue.	Blue.	Orange.	Orange.
Carmoisin	Violet.	Lilac.	Black.	Black.	Brown.	Pink.
Primuline Red	Brown.	Brown.	Black.	Violet.	Brown-red.	....
Polychromine	Brown.	Brown.	Black.	Violet.	Brown-red.	....
Orseillin BB	Black.	Blue.	Blue-black.	Blue.	Violet.	Violet.
Congo Red	Black.	Colourless.	Black.	Blue.	No change.	....
Benzopururin B	Brown.	Colourless.	Black.	Blue.	No change	....
Benzopurpurin 10 B	Black.	Colourless.	Black.	Blue.	No change.	....

RED COLOURS.—*Continued.*

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Decolourised.	....	Yellow.	Decolourised.	Decolourised by sodium sulphide.
Decolour.	....	Yellow.	Little change.	
....	Pink.	Blue.	Decolourised.	
No change.	....	....	Bluer.	
Yellow.	Yellow fluor.	Yellow.	Yellow.	
Pink.	Pink fluor.	Yellow.	Decolourised.	
Pink.	Pink.	Yellow.	Yellow.	Colour, extracted by ammonium acetate.
Orange.	Pink.	Yellow, red rim.	Orange.	
Bluer.	Pink.	Yellow.	Brighter.	Stands boiling with soap.
....	Red.	....	Yellow.	
Blue.	....	Dark blue.	Brown.	The spot with HNO_3 finally changes to yellow, with green rim.
No action.	No action.	Blue to brown.	Decolourised.	HNO_3 spot has a blue rim.
No action.	No action.	Blue to yellow.	Decolourised.	
No action.	No action.	Blue to brown.	Decolourised.	HNO_3 spot has a black rim.
Paler.	Pink.	Violet to yellow.	Decolourised.	
No change.	No change.	Violet to yellow.	Decolourised.	
No change.	No change.	Violet to brown.	Decolourised.	HNO_3 spot has a blue rim.
No change.	Pink.	Violet.	Decolourised on boiling.	HNO_3 spot disappears on washing.
No change.	....	No change.	Bright red-brown.	
No change.	....	No change.	Bright red-brown.	
Violet.	Violet.	Violet.	Decolourised.	HNO_3 spot disappears on washing.
No change.	....	Black.	Black, then decolourised.	HNO_3 spot restored to red by NH_3.
No change.	....	Brown.	Decolourised.	Picric acid turns the fibre brown.
No change.	....	Yellow.	Decolourised.	Picric acid turns fibre dark brown.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide.	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Deltapurpurin G.....	Black.	Colourless.	Black.	Blue.	No change.	....
Deltapurpurin 5 B....	Brown.	....	Blue.	Blue.	No change.	....
Brilliant Congo.......	Black.	Colourless.	Blue.	Blue.	No change.	....
Rosazurin B.........	Green.	Colourless.	Blue.	Blue.	No change.	....
Congo. Corinth.......	Black.	....	Black.	Blue.	Redder.	Colourless.
Hessian Purple B.....	Gray.	Colourless.	Blue.	Blue.	No change.	Pink.
Hessian Purple N....	Black.	Colourless.	Black.	Blue.	No change.	....
Azarine S............	Red.	Colourless.	Darker.	Red.	Bluer.	Red.
Azo-eosin............	Dark red violet.	Lilac.	Dark red-violet.	Lilac.	Orange.	....
Alizarin..............	Yellow.	Yellow.	....	Red.	Violet.	Violet.
Alizarin S............	Orange.	Orange.	Orange.	Orange.	Violet.	Violet.
Alizarin Maroon (with chrome).	Yellow.	Yellow.	Brown.	Brown.	Violet.	Violet.
Purpurin.............	Maroon.	Red.	Crimson.	Crimson.	Purple.	Pink.
Rose Bengal.........	Decolour	....	Brown.	....	Darker.	....
Rose Bengal B.......	Decol.	....	Scarlet.	Orange.	Darker.	....
New Magenta........	Yellow.	Yellow.	Yellow.	Yellow.	Decolour	....
Scarlet R......	Duller.	Pink.	....	Pink.	Yellower	....
Brilliant Double Scarlet 3 R.	Violet.	....	Violet.	Violet.	Darker.	....
Brilliant Scarlet R....	Darker.	Pink.	Crimson.	Crimson.	Brown.	....
Brilliant Scarlet......	No change.	....	Purple.	Purple.	Brown.	Brown.
Bordeaux Extra......	Violet.	....	Violet.	Violet.	Maroon.	Brown.
Bordeaux G.........	Violet.	Blue.	Blue.	Blue.	Purple.	....

Ammonia		Spot with nitric acid.	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution.			
No change.	....	Yellow.	Darker, then decolourised.	Picric acid turns fibre brownish-red.
No change.	....	Decolourised.	Decolourised.	
No change.	....	Blue.	Decolourised.	Picric acid turns fibre brown.
No change.	....	Brown.	Decolourised.	
Redder.	Pink.	Brown.	Decolourised.	Fibre black with HNO_3.
No change.	Pink.	Yellow.	Decolourised.	HNO_3—violet.
No change.	....	Brown.	Decolourised.	HNO_3—black.
Bluer.	Red.	Orange.	Yellow.	Picric acid—brown.
Orange.	Orange.	Brown.	Decolourised on heating.	HNO_3 spot disappears on washing.
No change.	No change.	Yellow.	Yellow.	$Ba(OH)_2$—violet. Gives no fluores. sol. with $Al_2(SO_4)_3$ on boiling (distinction from madder and purpurin).
Violet.	Colourless.	Yellow.	Orange, turned violet by NaOH.	Ash contains Al or Cr.
No change.	No change.	Brown.	Red on heating.	Ash contains Cr.
No change.	Pink.	Yellow.	Red, liquid yellow.	$Ba(OH)_2$—red. Fluores. sol. with boiling solution of $Al_2(SO_4)_3$.
No change.	Pink.	Yellow.	Decolourised.	
Darker.	Pink.	Yellow.	Decolourised.	
Decolour.	....	Yellow.	Decolourised.	
Brighter.	....	Yellow.	Decolourised.	
Pink.	....	Yellow.	Decolourised.	
No change.	Pink.	Yellow.	Decolourised.	
Darker.	Pink.			
Crimson.	Pink.	Yellow; blue rim.	Bluer.	
Darker.				

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Brilliant Croceine. . .	Purple.	Blue.	Violet.	Violet.	Purple.	....
Azo-carmine	Darker.	Red.	Green.	Green.	Maroon.	....
Azo-fuchsine G.	Brighter	Pink.	Violet.	Black.	Violet.	Violet.
Azo-fuchsine B.	No change.	Pink.	Crimson.	Red.	Red.	....
Alizarin GG (Cr mordant).	Brown.	Yellow.	Crimson.	Crimson.	Maroon.	....
Alizarin V (Cr mordant).	Brown.	Yellow.	Crimson.	Crimson.	Darker.	....
Alizarin Bordeaux B (Cr mordant).	Maroon.	Brown.	Violet.	Violet.	Violet.	Blue.
Brilliant Congo R. . .	Brown.	Colourless.	Blue.	Blue.	Yellower.	....
Benzo-Purpurin 4 B.	Blue.	Colourless.	Blue.	Blue.	No change.	....
Brilliant Purpurin R.	Blue.	Colourless.	Blue.	Blue.	No change.	....
Crystal Scarlet.	Crimson.	....	Violet.	Violet.	Brown.	....
Crocein Scarlet 3 B. .	Blue.	Blue.	Blue.	Blue.	Purple.	....
Croceine 3 BX.	Crimson.	Pink.	Purple.	Purple.	Brown.	....
Cochineal Red A. . .	Darker.	....	Crimson.	....	Brown.	Brown.
Cochineal Red 3R. .	Purple.	Purple.	Purple.	Purple.	Brown.	Brown.
Cyanosin.	Orange.	....	Orange.	....	No change.	....
Cyclamin.	Flesh.	....	Brown.	Brown.	....	....
Cloth Red G.	Violet.	Blue.	Violet.	Blue.	Darker.	....
Cloth Red B.	Violet.	....	Blue.	Black.	Crimson.	....
Cloth Red 3 G. . . .	Violet.	....	Blue.	Black.	Darker.	....
Clayton Cloth Red. .	Crimson.	....	Purple.	Violet.	Crimson.	....
Congo Corinth G. . .	Blue.	Colourless.	Blue.	Blue.	Redder.	Colourless.
Congo Corinth B. . .	Purple.	Colourless.	Blue.	Blue.	Redder.	Colourless.
Crocein Scarlet 3 B. .	Blue.	Blue.	Blue.	Blue.	Decolourised.	Gray.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid.	Remarks
Fibre	Solution			
Bluer.	....	Blue.	Decolourised.	
Bluer.	Pink.			
Scarlet.	Red.	Orange.	Decolourised.	
Red	Orange.	Red.	Decolourised.	
Maroon.	Colourless.	Orange.	Darker.	
Darker.	Colourless.	Orange.	Brown.	
Violet.	....	Red.		
No change.	....	Red.	Decolourised.	
No change.	....	Yellow.	Decolourised.	
No change.	....	Yellow.	Decolourised.	
....	Pink.	Yellow.		
....	Pink.	Yellow; blue rim.	Decolourised.	
Browner.	....	Yellow.	Decolourised on boiling.	
....	Pink.	Yellow.		
....	Pink.	Yellow; violet rim.	Lighter.	
No change.	....	Yellow.	Orange.	
....	Pink.	Yellow.	Decolourised.	
Darker.	....	Red.		
Crimson.	Pink.	Yellow.	Bluer.	
Brighter.	....	Yellow; purple rim.		
Brighter.	Pink.	....	Darker.	
Brighter.	Pink.	Brown.	Decolourised.	
Redder.	Pink.	Brown.	Decolourised.	
Lighter.	Scarlet.	Blue to yellow.	Decolourised.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Congo Red 4 R....	Blue.	Colourless.	Blue.	Blue.	No change.	....
Diamine Fast Red..	Violet.	Colourless.	Purple.	Blue.	Brown.	Colourless.
Diamine Scarlet B..	Violet.	Violet.	Violet.	Violet.	Orange.	Colourless.
Diamine Red NO...	Olive.	Colourless.	Blue.	Blue.	No change.	......
Diamine Red 3 B...	Yellow.	Colourless.	Blue.	Blue.	No change.	....
Erica B............	Redder.	Colourless.	Purple.	Violet.	Bluer.	Colourless.
Fast Red A........	Purple.	....	Violet.	Violet.	Maroon.	....
Fast Red B........	Crimson.	Pink.	Violet.	Purple.	Red.	....
Fast Red C........	Darker.	Pink.	Violet.	Violet.	....	....
Fast Red D........	Darker.	Pink.	Violet.	Violet.	Brown.	....
Fast Red E........	Maroon.	Pink.	Purple.	Purple.	Brown.	....
Fast Red BT.......	Darker.	....	Violet.	Violet.	Red.	....
Fluorescein........	Yellow.	Yellow.	Yellow.	Yellow.	....	Yellow; green fluor.
Geranin...........	No change.	....	Crimson.	Pink.	Violet.	Colourless.
Phloxin 2 B........	Red.	....	Brown.	....	Darker.	....
Scarlet 6 R........	Crimson.	Pink.	Violet.	Violet.	Brown.	....
Scarlet GG.........	....	Pink.	Darker.	Scarlet.	Orange.	....
Scarlet S extra......	Brown.	Blue.	Bluer.	Blue.	Violet.	....
Milling Red R......	Maroon.	....	Purple.	Purple.	Redder.	....
Orchil Red.........	Violet.	....	Blue.	Blue.	Maroon.	....
Scarlet 2 S........	Yellow.	Pink.	Orange.	Pink.	Orange.	....
Palatine Scarlet....	Darker.	Pink.	Crimson.	Magenta.	Brown.	....
Palatine Red.......	Bluer.	....	Blue.	Blue.	Brown.	Brown.
Roxamine..........	Bluer.	....	Violet.	Violet.	Purple.	....
Safrosine..........	Decolour.	....	Yellow.	Yellow.	Darker.	....
Orchil Substitute V.	Crimson.	Crimson.	Crimson.	Crimson.	Maroon.	....
Orchil Substitute 3 VN.	Crimson.	Crimson.	Crimson.	Crimson.	Maroon.	....
Fast Violet B. (Violamin B.)	Violet.	....	Scarlet.	Red.	Violet.	....
Fast Violet R. (Violamin R.)	Bluer.	Pink.	Red.	Red.	Red.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
No change.	Pink.	Orange.	Decolourised.	
No change.	....	Brown.	Decolourised.	
Orange.	....	Crimson.	Decolourised.	
No change.	Pink.	Brown.	Decolourised.	
No change.	Pink.	Brown.	Decolourised.	
No change.	Pink.	Red.	Decolourised.	
Darker.	....	Yellow.	Lighter.	
....	....	Yellow.	Lighter.	
Brighter.	Pink.	Yellow.	Lighter.	
Darker.	Brown.	Yellow.	Lighter.	
Darker.	Red.	Yellow.	Brighter.	
Darker.	....	Yellow.	Lighter.	
....	Yellow, green fluor.	....	Yellow.	
Violet.	Violet.	No change.	Decolourised.	
Darker.	Pink.	Yellow.	Decolourised.	
....	Pink.	Yellow.		
....	Pink.			
Bluer.	Pink.	Yellow.	Crimson.	
No change.	....	Orange.		
Crimson.	....	Orange.		
Yellower.	....	Yellow.		
Lighter.	....	Yellow.		
Redder.	....	....	Decolourised.	
Purple.	....	Yellow.	....	HNO_3—blue rim.
Darker.	Pink.	Yellow.	Decolourised.	
Maroon.	....	Yellow.	Lighter.	
Maroon.	....	Yellow.	Lighter.	
Redder.	Pink.	Scarlet.		
....	Pink.	Scarlet.		

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Orchil Red G.........	Crimson.	Pink.	Purple.	Purple.	Darker.	....
Naphthylene Red....	Green.	Colourless.	Blue.	Blue.	No change.	....
St. Denis Red........	Bluer.	Colourless.	Crimson.	Crimson.	Orange.	Orange.
Poppy 2 R. Xylidine Red.	....	Red.	Darker.	Red.	Decolourised.	Red.
Poppy 3 R. Cumidine Red.	Red.	Red.	Darker.	Red.	Brown.	Brown.
Wool Scarlet R	Darker.	Rose.	Darker.	Red.	Orange.	Red.
Pyrotin R PO........	Violet.	Colourless.	Violet.	Violet.	Brown.	Brown.
Ponceau 6 R.........	....	Violet.	Violet.	Magenta.	Brown.	Brown.
Tolylene Red. Neutral Red.	Blue.	Blue.	Green.	Green.	Olive.	....
Pyronin B...........	Orange.	Orange.	Orange.	Orange.	Orange.	Colourless.
Stilbene Red.........	Black.	Colourless.	Violet.	Colourless.	....	Pink.
Alkali Red...........	Blue.	Colourless.	Blue.	Blue.	....	Pink.
Chromotrope 2 R....	No change.	Pink.	Dark red.	Dark red.	Redder.	Pink.
Titan Scarlet.........	Dark red.	Dark red.	Magenta.	Magenta.	Dark red.	Red.
Atlas Red...........	No action.	Colourless.	Crimson.	Crimson.	No action.	....
Dianthin	Darker.	....	Crimson.	Crimson.	Orange.	....
Ingrain Maroon......	No change.	....	Maroon.	Maroon.	No change.	....
Acid Milling Scarlet..	Brownish.	Colourless.	Maroon.	Maroon.	Darker.	....
Rock Scarlet SY.....	Brownish.	Colourless.	Maroon.	Maroon.	No change.	....
Rock Scarlet BS.....	Browner.	Colourless.	Maroon.	Maroon.	No change.	....
Clayton Cloth Scarlet.	Darker.	Magenta.	Magenta.	Ruby.	Maroon.	Reddish.
Cochineal Scarlet G..	Brownish.	....	Bluer.	....	Orange.	Orange.
Cochineal Scarlet R..	Brownish.	....	Purple.	Colourless.	Orange.	Orange.
Cochineal Scarlet 2 R.	Brownish.	....	Purple.	Colourless.	Orange.	Orange.
Wool Scarlet G.......	No change.	....	No change	....	Orange.	Orange.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Bright.	Red.	Yellow.		
No change.	....	Green.	Decolourised.	
Orange.	Orange.	No change.	Decolourised.	
Brighter.	....	Yellow.	Decolourised.	
No change.	No change.	Yellow.	Decolourised.	
Orange.	Red.	Darker.		
....	Orange.	Blue.	Decolourised.	Colour extracted with hot $NH_4C_2H_3O_2$ solution.
....	Violet.	Scarlet.	Decolourised.	Colour extracted with hot $NH_4C_2H_3O_2$ solution.
Orange.	Orange.	Blue.	Decolourised.	Colour extracted by hot $NH_4C_2H_3O_2$ solution.
Brighter.	Yellow.	Scarlet.	Decolourised.	Colour extracted by hot $NH_4C_2H_3O_2$ solution.
....	Pink.	Violet.	Decolourised.	
....	Orange.	Olive.	Decolourised.	
Lighter.	Pink.	Yellow.	Decolourised.	Boiled with alum—violet.
....	Orange.	Orange.	Decolourised.	
No change.	Brown.	Brown.	Yellow.	On reduction it gives primuline.
Paler.	Orange.	Darker.	Decolourised.	
....	Pink.	Maroon.	Yellow.	On reduction it gives primuline.
Paler.	Orange.	Yellow.	Pink.	
No change.	....	Yellow.	Decolourised.	Resists boiling soap solution.
No change.	Pink.	Yellow.	Decolourised.	Resists boiling soap solution.
....	Pink.	Yellow.	Decolourised.	
Yellower.	Orange.	Yellow.	Decolourised.	
Yellow.	Orange.	Yellow.	Decolourised.	
Yellow.	Yellow.	Yellow.	Decolourised.	
Yellower.	Yellow.	Yellow.	Decolourised.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Wool scarlet R.	No change.	....	No change.	....	Orange.	Orange.
Wool Scarlet 2 R.	No change.	....	No change.	....	Orange.	Orange.
Buffalo Rubine	Violet.	....	Blue.	Violet.	Ruby.	Ruby.
Cotton Scarlet 3 B.	Violet.	....	Violet.	Colourless.	Violet.	Violet.
Brilliant Red	Violet.	....	Violet.	Colourless.	Brownish.	Brown.
Madder	Brown-red.	....	Brown-red.	Red.	Purple.	Purple.
Orchil	No change.	Red.	Purple.	Purple.	Purple.	....
Brazil wood	Dark red.	Pink.	Brown.	Yellow.	Maroon.	Violet.
Barwood	Redder.	....	Red-brown.	Dirty brown.	Purple.	Colourless.
Sanderswood	Browner.	....	Red-brown.	Red-brown.	Purple.	Colourless.
Safflower	Decolourised.	....	Decolourised.	....	Pale yellow.	....
Cochineal	Orange.	Orange.	Pink.	Pink.	....	Purple.
Ammoniacal cochineal.	Orange.	Orange.	Yellow-brown.	....	Bluer.	....
Brilliant Orseille C.	Green. Restored on dilution	....	Green. Pink on dilution.	....	Dull green.	Light blue.
Tannin Orange R.	Orange on dilution. Crimson.	....	Crimson.	Orange on dilution.	....	Dirty orange.
Alkali Fast Red R.	Reddish-brown. Restored on dilution.	....	Reddish-brown. Red on dilution.	....	Rather duller.	Pink.
Diamine Rose B. D.	Redder.	....	Bluer.	....	Bluer.	....
Mars Red G.	Little change.	....	Red violet. Red on dilution.	....	....	Scarlet.
Sorbine Red	....	Scarlet.	....	Bluish-scarlet.	Red orange.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Yellower.	Yellow.	Yellow.	Decolourised.	
Yellower.	Yellow.	Yellow.	Decolourised.	
Dull red.	Red.	Yellow.	Decolourised.	
Violet.	....	Orange.	Decolourised.	
No change.	....	Orange.	Decolourised.	
Brown-red.	....	Yellow.	Terra-cotta.	
Purple.	....	....	Decolourised.	Ash contains Al.
Violet.	Violet.	Yellow.	Violet.	
Purple.	Colourless.	Olive.	No change.	
Purple.	Colourless.	Olive.	No change.	$FeSO_4$—violet.
Pink.	....	....	Yellow.	On cotton fibre.
....	Purple.	Yellow.	Orange.	Sn mordant.
Violet.	....	....	....	Ash contains Al.
Little change.	....	Green.	Decolourised.	Acid colouring matter for wool.
....	Light orange.	Red orange.	Decolourised.	Form of paste. For calico printing. Silk (soap bath), leather, paper and cotton (reactions for cotton).
Little or no change.	....	Brown orange.	Decolourised.	Not dyed in alkaline bath but in the usual way with H_2SO_4 and Glauber's salt. Wool colour.
....	....	Scarlet.	Decolourised.	Diamine colour on cotton, and wool. For dyeing and padding, and for printing pale shades.
....	....	Yellow.	Decolourised.	Acid colour, similar to Naphthol Red but more fiery and brilliant. Reactions, on wool.
....	....	Yellow orange.	Decolourised.	Acid colouring matter, wool. Suitable for producing "shot" effects in the dying of gloria cloth.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Rosophenine Pink 10 B.	Bluish-pink. Restored on diluting.	....	Bluish-crimson. Pink on diluting.	....	Bluer.	....
Alkali Crimson 161.	Redder.	....	Blue. Pink on dilution.	....	Brighter	....
Chlorantine Red 4 B.	Brown. Restored on dilution.	....	Dirty blue.	....	Yellower.	....
Rosophenine-geranine.	Bluer.	....	Bluer. Dull pink on dilution.	....	Bluer.	....
Nile Scarlet YY....	Dull red.	....	Crimson. Pink on dilution.	....	Orange.	....
Direct Fast Scarlet R.	No change.	Colourless.	Bluer.	Bluish-red.	No change.	Slightly yellowish-red.
Diamine Fast Scarlet 4 BN.	Unchanged.	Colourless.	Unchanged.	Colourless.	Lighter.	Red.
Oxy Chrome-Garnet B.	Lighter.	Pink.	No change.	Colourless.	Crimson.	Crimson.
Algole Scarlet G....	No change.	Colourless.	No change.	Reddish.	No change.	Colourless.
Diamine Azo Scarlet 4 B.	No change.	Colourless.	Little change.	Pink.	Lighter.	Pink.
Diamond Red G....	Orange.	Orange.	Orange.	Orange.	Crimson.	Crimson.
Dianil Fast Scarlet 6 BS.	Much darker.	Colourless.	Violet.	Violet.	Darker.	Yellowish.
Ciba Scarlet G.....	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.
Azo Fuchsine 4 G extra.	Yellower.	Red.	Bluish-crimson.	Crimson.	Reddish-brown.	Red.
Oxamine Red 3 B..	Purple.	Colourless.	Blue.	Colourless.	No change.	....
Benzo Fast Scarlet 7 BS.	Dark brown.	Colourless.	No change.	Colourless.	Darker in shade.	Slight orange.
Erio-chrome Red B.	Bright red.	Colourless.	Bright red.	Colourless.	Lighter.	Colourless.
Trona Red B 3.....	No change.	....	....	Light red.	....	Orange.

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
....	....	Pale pink. Colourless on dilution.	Decolourised at once.	Dyed on flanelette. Good fastness to acids, alkalies and air.
....	....	Brown.	Decolourised.	Direct dyeing cotton colour.
		Greenish-yellow.	Yellowish-brown.	Direct cotton colour (and for wool). Recommended for cop dyeing.
		Slowly decolourised.	Slowly decolourised.	A dyestuff for cotton giving full shades at 0.25%.
....	....	Orange. Solution pink.	Very slowly decolourised.	Dyed in an acid bath. Suitable for wool and carpet yarn.
....	....	No change.	Decolourised on boiling. Solution colourless.	Direct cotton colour.
....	....	Unchanged.	Light red on boiling. Solution colourless.	Direct cotton. Exhausts well.
....	....	Redder. Soln. Red.	Light red on boiling. Solution red.	Acid mordant wool dye.
....	....	Orange.	No change on boiling.	Vat dye, very soluble.
....	....	Lighter.	Little change on boiling.	Direct cotton dye.
....	....	Yellow.	Light red on boiling. Solution red.	Acid mordant dye.
....	....	Yellower.	Little change on boiling. Solution colourless.	Direct cotton dyestuff.
....	....	No change.	No change on boiling.	Vat dye. Animal fibres may also be dyed.
....	....	Orange.	Decolourised on boiling.	Acid dye for wool.
....	....	Purplish-grey.	A little bluer on boiling.	Direct cotton, suitable for mixed fabrics.
....	....	Orange.	Darker on boiling. Solution colourless.	Direct cotton dye, loose cotton, yarn, and pieces. especially for mercerised material.
....	....	Orange.	Bright red on boiling. Solution pink.	Acid mordant dye.
....	....	Pink solution	Decolourised on boiling.	Cotton.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Alizarin Red PS....	Bleeds slowly.	....	....	Purple.	....	Dirty dark purple.
Benzo Red, SG.....	Dark red.	....	Dark red.	....	....	Red.
Pyramine Orange R.	Red.	....	Light brown.	....	Darker.	....
Irisamine G........	Yellow (restored on washing).	....	Decolourised.	....	Slightly bluer.	....
Rhodamine 6 G, extra.	Orange (col. restored on washing).	....	Orange.	....	Redder.	....
Columbia Fast Scarlet.	Dark yellowish-brown.	....	Deep blue.	....	No change.	Pale red on boiling.
Acid Rhodamine R..	Red.	....	Reddish-yellow.	....	Colour partially stripped.	....
Benzo Fast Red GL.	Reddish-blue.	....	Blue.	....	Unchanged.	Slightly pink on heating.
Anthracene Chrome Red A.	Browner.	....	Brown.	....	....	Slight pink on heating.
Acid Alizarin Red B.	Red.	Colourless.	Red.	Pink.	Scarlet.	Colourless.
Chloranisidine P....	Brown.	Colourless.	Destroyed.	Purple.	No change.	....
Azo-phloxine.......	No change.	....	Decolourised to buff.	Colourless.	Lighter.	Colourless.
Amido Naphthol Red 2 B.	Redder.	Red.	Redder.	Red.	Orange.	Orange.
Acid Eosin 5 B.....	Crimson.	Colourless.	Dark crimson.	Colourless.	Orange.	Pale orange.
Palatine Chrome Red B.	Little change.	Pale red tint.	Red.	Pink.	Reddish-brown.	Pale red.
Palatine Chrome Claret.	Little change.	Pale red.	Dark yellowish-brown.	Dark yellowish-brown.	Lighter.	Red tint.
Triazol Red 10 B...	Dark blue.	Colourless.	Dark blue.	Dark blue.	No change.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
		Light yellow.	Slowly decolourised.	Mordant dyes all fibres.
		Bleeds slightly.	Light yellowish-brown.	Direct cotton red.
		Light brown.	Decolourised.	Direct cotton.
		Decolourised	No effect.	Basic colour. Cotton or silk.
		Orange.	No effect.	Basic dye for dyeing or printing.
		Reddish brown.	No effect.	Direct cotton red.
		Yellowish-red.	Partially decolourised.	Brand of rhodamine.
		Darker. Solution bright red.	No change.	Direct cotton for wool, silk or union fabrics.
		Yellow solution on heating.	No change.	Acid mordant.
		Red. solution pink.	Lighter and redder on warming. Pink solution.	Acid mordant.
		Slightly browner. Pale pink solution.	Slightly redder on boiling.	Yellower and more brilliant scarlet then nitrosamine red.
		Yellowish orange. Soln. pale orange.	Decolourised on warming.	Acid dye.
		Orange red. Soln. red.	Pale red on boiling. Solution red.	Level dyeing acid dyestuffs.
		Orange. Solution pale yellow.	Decolourised.	Easily leveling acid dye. White discharges with tin and Zn.
		Red. solution pink.	Pink on heating. Solution pale pink	Acid mordant. Good fastness to milling.
		Orange. Solution orange.	Nearly decolourised.	Acid mordant. Fast to light, milling, etc.
		Dark red. Solution red.	No change.	Soluble and level dyeing direct cotton dyestuff.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Mercerine Wool Red Y.	Yellow.	Pale yellow.	Orange.	Pale orange.	Crimson.	Colourless.
Toluylene Bordeaux B.	Deep dull blue.	Colourless.	Deep blue.	Bright blue.	No change.	....
Acid Anthracene Red 3 B.	Bluish-crimson.	Colourless.	Bright purple.	Pale purple.	No change.	....
Oxamine Fast Red F.	Dull reddish-blue.	Colourless.	Bright reddish-blue.	Bright reddish-blue.	No change.	....
Milling Scarlet B ...	Turns bluer.	Colourless.	Crimson.	Crimson.	Turns yellower.	Orange-yellow.
Ciba Bordeaux B...	Unchanged.	Colourless.	Brown.	Brown.	Unchanged.	Colourless.
Vat Red...........	Maroon.	Colourless.	Red.	Colourless.	Red.	Colourless.
Diazo Brilliant Scarlet PR extra.	Much darker.	Colourless.	No change.	Colourless.	No change.	Colourless.
Triazol Bordeaux B.	Reddish-blue.	Colourless.	Violet-blue.	Violet-blue.	No change.	....
Wool Red SB......	Scarlet.	Colourless.	....	No change.	Pale scarlet.	Colourless.
Diamine Brilliant Bordeaux R.	Deep blue.	Colourless.	Deep blue.	Colourless.	No change.	....
Duatol Bordeaux B.	Blue.	Colourless.	Blue-black.	Colourless.	Red.	Colourless.
Algole Bordeaux, 3 B paste.	Little change.	Colourless.	Little change.	Maroon.	No change.	Colourless.
Lanafuchsine BBS..	Brownish-red.	Colourless.	Blue.	Blue.	Brownish-red.	Pale red.
Algole Orange R....	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Pale yellow. Solution yellow.	Orange yellow on warming. Solution pale yellow.	Acid dye. Fast to light, and milling.
....	....	Deep purple. Soln. pale crimson.	No change.	Direct cotton dyestuff. Resists feeble chloring.
....	....	Bluish crimson, then orange, to orange-yellow. Soln. pale orange.	Little change.	Acid dye for wool.
....	....	Deep orange brown. Soln. orange.	No change.	Direct cotton dyestuff. Suitable for cotton, wool, silk and unions.
....	....	Turns yellower. Soln. pale scarlet.	Pale bluish-crimson on warming.	Bright scarlet shades in an acid bath, which are fast to light, etc.
....	....	Brown.	Decolourised. Solution colourless.	Vat dyestuff. Great fastness.
....	....	Red. Solution colourless.	Red on boiling. Solution colourless.	Sulphur derivative of indigo.
....	....	Darker. Soln. colourless	On boiling, lighter. Solution colourless.	Direct cotton.
		Fibre and solution, purple.	On warming, a little paler.	Direct cotton.
....	....	Yellow. Soln. pale yellow.	Decolourised on warming.	Acid dyestuff.
....	....	Reddish-brown. Soln. colourless.	Purple.	Direct cotton.
....	....	Reddish-orange.	Decolourised.	For self shade or union.
....	....	Yellow.	No change.	Vat dye for cotton.
....	....	Bright red. Soln. pale red.	Decolourised on boiling.	Level dyeing acid colouring matter. For mixture shades and cotton effects.
....	....	No change. Soln. colourless.	On boiling, no change. Soln. colourless.	Vat dye for cotton. Fast against washing, chlorine, etc.

VII. BLACK COLOURS.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Tannin Black........	Straw.	....	Straw.	....	Grey.	....
Naphthol Black..	....	Reddish.	....	Olive-green.	....	Reddish.
Brilliant Black......	....	Violet.	....	....	Greener.	Violet.
Resorcin Black......	Grey.	Brown.	Brown.	Brown.	....	Green.
Wool Black..........	Black.	Blue.	Black.	Blue.	No action.	....
Aniline Black........	No action.	....	No action.	....	No action.	....
Alizarin Black........	Orange.	....	Orange.	....	No action.	....
Alizarin Black........	Black.	Violet.	Black.	Blue.	Black.	Blue.
Woaded Black.......	Blue.	Violet.	Blue.	Violet.	Blue.	Violet.
Logwood Black......	Brown.	Red.	Brown.	Red.	....	Purple.
Naphthol Black B....	No change.	....	Green.	Blue.	No change.	....
Naphthol Black 3 B...	....	....	Green.	Blue.	....	....
Naphthol Black 6 B...	Redder.	Colourless.	Greener.	Greenish.	....	....
Naphthyl-amine Black D.	No change.	Green.	....	Violet.	Bluer.	Blue.
Anthracite Black D...	Violet.	....	Greener.	Grey.	No change.	Pink.
Victoria Black 5 G...	Greener.	Colourless.	....	Green.	Dark green.	Green.
Victoria Black Blue...	....	....	....	Green.	Greener.	Violet.
Jet Black R..........	....	Green.	Blue.	Blue.	Dark green.	....
Wool Gray...........	Lighter.	Maroon.	Maroon.	Grey.	Brown.	....
Diamond Black.......	Green.	....	Greener.	Green.	Darker.	Grey.
Nigrosine, soluble.....	Slate.	....	Slate.	Grey.	Brown.	....
Nigrosine..............	Darker.	Purple.	Violet.	Blue.	Maroon.	....
Benzo Black S	Violet.	....	Violet.	Violet.	Violet.	Red.
Benzo Blue Black R..	....	....	Blue.	Blue.	Violet.	....
Violet Black..........	Bluer.	....	Blue.	Blue.	....	Pink.

VII. BLACK COLOURS.—*Continued.*

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
No action.	....	....	Decolourised.	Ash contains Fe.
No action.	....	Brown.	Decolourised.	
....	Violet.	Brown.	Decolourised.	
No action.	....	Yellow.	Brown.	Ash contains Fe.
No action.	....	Red-brown..	Decolourised.	
No change.	....	....	Green-grey.	$CaOCl_2$—brown-red.
No action.	....	....	Orange.	Ash contains Fe.
No action.	....	Olive-green.	Brownish.	
Blue.	Violet.	....	Green-blue.	
....	Purple.	....	Violet.	Ash contains Fe or Cr.
Violet.	Violet.	Red.	Crimson.	
Violet.	Violet.	Red.	Crimson.	
....	Blue.	Red.	Purple.	
....	Violet.	Brown.	No change.	
....	....	Yellow.	Violet.	
....	Violet.	Red.	Decolourised.	
....	Violet.	Orange.		
....	....	Yellow.	Decolourised.	
Brown.	....	Yellow.	Violet.	
....	Grey.	Red.	....	Ash contains Cr.
Brown.	Grey.			
Maroon.				
Violet.	Pink.	Scarlet.	Decolourised.	On cotton.
Violet.	Pink.	Brown.	Decolourised.	On cotton.
....	Violet.	Orange.	Decolourised.	On cotton.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Benzo Grey S........	Bluer.	....	Violet.	Blue.	Violet.	....
Diamine Black BO....	Redder.	....	Blue.	Blue.	Redder.	Pink.
Same developed with phenylene-diamine	....	....	Blue.	....	....	....
Diamine Black RO....	Redder.	....	Blue.	Blue.	Violet.	Pink.
Same developed with phenylene-diamine.	....	....	Darker.	....	....	....
Diazo Black R (with β-naphthol).	....	....	Navy blue	Navy blue.	....	Rose.
Diazo Brilliant Black B.	Greenish blue.	....	Indigo blue.	Indigo blue.	....	....
Diamine Deep Black OO.	Dark violet.	Dark violet.	Dark blue.	Blue.	Red.	Red.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Benzo Grey.........	Darker.	....	Greenish-grey; dirty purple on dilution.	....	....	Light brown.
Alizarin Blue-Black B.	Little or no change.	....	Violet.	....	Little or no change.	....
Direct Deep Black G.	Little change.	Light red.	Dull violet.	....	....	Violet.
Vidal Black........	Little change.	Faintly yellow.	Dull violet.	....	Bluish-green.	....
Diamine Grey G....	Little change.	....	....	Grey.	Little change.	....
Diamin Jet Black, CR.	Little action.	....	Dull dark violet.	....	....	Light violet.
Oxydiamine Black, NF.	....	Light brown.	Dark reddish blue. Dull violet on dilution.	....	....	Red-violet.
Cross Dye Black....	....	Light yellow.	....	Violet black.	....	Grey.

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Redder.	....	Scarlet.	Decolourised.	On cotton.
....	....	Violet.	Decolourised.	On cotton.
....	....	....	Decolourised.	On cotton.
....	....	Violet.	Decolourised.	On cotton.
....	....	....	Decolourised.	On cotton.
....	Rose.	Brown.	Decolourised.	
....	....	Violet.	Decolourised.	
....	Violet.	Brown.	Decolourised.	

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
....	Purple.	Light brown.	Decolourised.	May be combined with all direct cotton colours which are dyed with salt.
Little change.	....	Olive-brown.	....	Alizarin colour. Cotton printing with acetate of chromium, *wool*.
....	Dull volet.	Dark brown.	Decolourised.	Discharged with tin salts; slightly yellow shade, but zinc dust, good white.
....	....	Dull violet.	Drab.	Cotton colour. Fast to acids.
....	....	Brown.	Decolourised.	Cotton, silk, cotton and silk. Direct cotton colour.
....	....	Brown.	Greyish-yellow.	Cotton Colour.
....	....	Brown.	Slowly decolourised. Yellow liquid.	Easily discharged white in light shades. Reactions for dye on cotton.
....	....	Dark brown solution.	Dark grey.	Cotton colouring matter. Acts as a mordant for basic dyes.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Soudan Black......	. Dark violet.	Red.	Green. On dilution, violet.	....	....	Deep violet.
Paramine Blue-Black S.	Redder.	....	....	Reddish-blue. Violet on dilution.	Violet.	Bluish-red.
Janus Black I.....	Green. Blue on dilution.	....	Olive-green. Reddish-brown on dilution.	....	Blue-black.	....
Direct Deep Black E extra.	Little change.	....	Dark blue.	Dirty red on dilution.	Greener.	....
Clayton Fast Black D.	No change.	Tinged with yellow.	No change.	....	No change.	....
Diazo Black, 2 B...	No change.	....	Bluer.	Blue. Purple on dilution.	No change.	....
Clayton Fast Grey S.	Greenish.	....	Olive. Decolourised on dilution.	....	Little action.	....
Palatine Chrome Black 6 B.	No change.	Colourless.	Light blue.	Colourless.	Light blue.	Red.
Agalma Black B...	Violet.	Violet.	Dark crimson.	Crimson.	Greenish-blue.	Greenish-blue.
Diazo Fast Black, MG.	Little change.	Colourless.	Little change.	Brown.	Lighter in shade.	Faint red.
Oxychrome Black F	Bluer.	Colourless.	Maroon.	Greenish.	Violet.	Violet.
Kresol Black BB..	Reddish-violet.	Light red.	Reddish-violet.	Pink.	Violet.	Violet.
Acid Black 8 B.....	Violet.	Violet.	Bluer.	Bluish.	Green.	Green.
Duatol Black 3 B...	Little change.	Colourless.	Little change.	Colourless.	Blue.	Blue.
Acid Alizarin Black SNT.	No change.	Colourless.	Violet.	Violet.	Reddish-violet.	Reddish-violet.
Katigen Deep Black BG.	Little change.	Colourless.	Dark brown.	Brown.	No change.	Colourless.
Immedial Brilliant Black.	No change.	....	No change.	....	No change.	....

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
....	....	Scarlet.	Decolourised.	Acid black. Fast to light and milling. Penetrates thick material, *wool.*
....	....	Violet to crimson.	Slowly decolourised.	New cotton colour. May be diazotised on the fibre. Reactions for cotton.
....	....	Greenish-yellow. Yellow on dilution.	Brown.	Dyed on union lining.
....	....	Orange. Yellower on dilution.	Decolourised.	Very strong dyestuff. All kinds of cotton material, half wool in a neutral bath.
....	....	No change.	Olive-brown.	Similar in some respects to the Vidal class. Fast to acids, alkalies, light, and milling.
....	....	Solution and fibre reddish-brown.	Slowly decolourised.	Direct dyeing colour for cotton.
....	....	Little action.	Brownish-drab.	Dyestuff for cotton. Fast to atmospheric influences and light and all reagents.
....	....	Red.	Light blue on boiling. Solution colourless.	Acid mordant for wool.
....	....	Light brown.	Decolourised on boiling. Solution colourless.	Acid dyestuff for wool.
		Lighter in shade.	On boiling decolourised solution colourless.	Direct cotton. Capable of being diazotised and developed.
....	....	Reddish-yellow.	Decolourised on boiling.	Acid mordant for wool.
....	....	Dark red.	Light green on boiling. Solution colourless.	Acid dyestuff, suitable for piece goods and horse hair.
		Orange.	Decolourised on boiling.	Acid dye, for piece goods.
....	....	Reddish-orange.	Decolourised on boiling.	For self shade or unions.
....	....	Dark red.	No change on boiling.	Acid mordant for wool.
....	....	Claret.	Little lighter on boiling. Solution colourless.	Sulphide dye for cotton.
....	....	No change.	Dull bluish-green on warming.	Sulphide dyestuff. Jet black without after-treatment.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Thiogene Black. 6 BG conc.	Bluer.	Colour-less.	No change.	Colour-less.	Bluer.	Colour-less.
Diamine Fast Black X.	Bluer.	Violet.	No change.	Colour-less.	Bluer.	Blue.
Diamine Fast Grey RN.	Green.	Light green.	Violet.	Colour-less.	No change.	Colour-less.
Sulphocyanine Black 4 B.	Lighter.	Violet.	No change.	Colour-less.	Bluer.	Colour-less.
Erio-chrome Black T.	No change.	Colour-less.	Bluer.	Blue.	Brown.	Brown tint.
Naphthol Blue-Black BN.	Greenish-blue.	Greenish-blue.	Dark blue.	Dark blue.	Violet.	Violet.
Diamine Beta Black B.	No change.	....	....	Dark blue.	Bleeds slowly.	....
Immedial Black FF, extra.	No change.	....	....	Blue solution.	No change.	....
Pluto Black FR....	No change.	....	....	* Blue.	No change.	....
Benzonitrol Black.	Little change.	....	Blue.	....	No change.	....
Diamond Black 2 B.	Slightly greener.	....	Blue.	....	Slightly bluer.	....
Coomassie Wool Black 4 BS.	Dark bluish-purple.	....	Dark bluish-purple.	....	No effect.	....
Phenylamine Black T.	No effect.	....	Dark bluish-purple.	....	No effect.	....
Naphthalene Acid Black 4 B........	Slightly bluer.	....	Bluish-purple.	....	Lighter.	....
Phenylene Black 4 B	No effect.	....	Blue.	....	No visible change.	Pale blue.
Azo Acid Black 3 BL. extra.	Red.	....	Red.	....	Violet.	....
Oxamine Black N...	No change.	....	No change.	....	Partially stripped.	Deep blue.
Carbon Black BW.	Slightly paler.	....	As with HCl.	....	Colour partially removed.	....
Kryogen Black B...	No action.	Yellow.	No action.	First violet then brown	No action.	....
Alizarin Chrome Black S.	No change.	....	No effect.	....	No change.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	No change.	Decolourised on boiling.	Sulphide dye for silk and half silk.
....	....	Colour stripped.	Decolourised on boiling.	Direct cotton dyestuff.
....	....	Salmon.	Decolourised on boiling. Solution colourless.	Direct cotton dyestuff.
....	....	Light brown.	Grey on boiling. Solution colourless.	Suitable for dyeing dress goods and men's goods.
....	....	Brown.	Blue on boiling. Solution blue.	Acid mordant for wool.
....	....	Bright red.	Decolourised on boiling.	Level dyeing acid colouring matter.
....	....	Bluish-red solution.	No change.	Direct cotton developed.
....	....	Bleeds slightly.	Little change cold. Olive-brown on heating.	Sulphide black.
....	....	Reddish-brown.	Little change.	Direct black (union goods).
....	....	Maroon.	Slightly lighter.	Direct black.
....	....	Light brown.	Red first then decolourised.	Acid mordant dye.
....	....	Decolourised. Solution red.	Slowly decolourised.	Acid black.
....	....	Brown. Solution red.	Slowly decolourised.	Acid black.
....	....	Decolourised.	Lighter.	Acid black.
....	....	Brown.	No change. Solution blue on warming.	Acid black.
....	....	Red.	Red.	Acid black.
....	....	Pale red almost decolourised.	No change.	Direct-dyeing cotton.
......	....	Reddish colour extracted.	No effect.	Direct cotton black.
....	....	Decolourised. Solution maroon.	Green.	Sulphide colour.
....	....	Greyer.	No change.	Bisulphite compound.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hyrdoxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Chrome Patent Black DG.	No change.	....	No change.	....	Cold-no action. Colour removed on heating.	....
Diphenyl Black base I.	No change.	....	Unchanged.	Light blue.	No change.	....
Chromate Black T.	Dark reddish-brown.	....	Violet black.	....	Violet black.	....
Sulphur Black T extra.	No change.	....	No change.	....	No change.	....
Oxydiaminogene OT.	Unchanged.	Blue black.	Blue.	Blue.	No change.	....
Pyrol Black B....	No action.	....	Black.	Dull purple.	....	....
Thional Black FC.	No change.	....	No change.	Bluish-violet.	No change.	....
Azo Merino Black BE.	No action.	Pink.	No action.	....	No action.	....
Acid Alizarin Grey G.	No action.	....	Dark brown.	Colourless.	No action.	....
Domingo Chrome Black FF.	No change.	....	Black.	Blue.	Black.	Pale blue.
Domingo Blue-Black LW.	Scarlet.	Colourless.	Dark red.	Pale red.	Crimson.	Pale red.
Biebrich Acid Black ST.	No change.	Purple.	Little change.	Pale blue.	No change.	Pale blue.
Thion Blue Black.	No change.	....	Little change.	Violet.	No change.	....
Domingo Alizarin Black B.	No change.	....	Violet brown.	Pale purple.	No change.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Redder.	No change.	Acid mordant.
....	....	No change.	No change.	Analogous to aniline black ungreenable. Can be printed along with steam colours.
....	....	Browner.	Violet-black.	Acid mordant.
....	....	No change.	Green.	Sulphur black.
....	....	Fibre colourless; solution yellow.	No change.	Direct cotton dye.
....	....	Black. Solution purplish-brown.	On warming no change. Solution pale red.	Sulphur colour.
....	....	No change. Solution violet.	Olive-green on warming; black reproduced on washing.	Sulphur colour.
....	....	Brown. Solution orange-red.	Decolourised on boiling.	Acid dye.
....	....	Dark brown. Solution light brown.	No action.	May be dyed in a neutral bath, an acid bath with or without after-treatment, or upon chrome or alum mordant.
....	....	Reddish-orange. Solution orange.	No change.	Dyestuff for wool. Fast to light, milling, hot pressing, etc. Cotton effects remain unstained.
....	....	Yellow. Solution pale yellow.	Bright green on warming.	Dyestuff for wool. Cotton checking threads remain unstained.
....	....	Reddish-brown. Solution scarlet.	On warming, pale brown. Solution colourless.	For wool. Suitable for dyeing in an acid bath. Cotton effect remaining white.
....	....	Little change. Solution pale purple.	On warming, olive. Solution colourless.	Sulphide dyestuff. Suitable for dyeing cotton fabrics.
....	....	Reddish then orange. Solution reddish tint.	On warming, dull purple. Solution pale purple.	Acid mordant dye suitable for loose wool, piece goods, cotton effect fabrics and machine dyeing.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Wool Printing Black B.	No change.	....	Little change.	Pale dull blue.	Dark violet blue.	Pale violet blue.
Direct Black FF. extra.	No change.	....	Little change.	Orange-yellow.	No change.	....
Para Diamine Black B.	No change.	....	Little change.	Bright bluish-green.	No change.	....
Corvan Black B..	No change.	....	Little redder.	Colourless.	No change.	....
Chrome Acid Black G.	No change.	....	Deep bluish-crimson.	Pale crimson.	Little change.	Purple.
Union Black 2 BNI.	Violet.	Colourless.	Deep blue.	Blue tint.	Little change.	Colourless.
Benzyl Acid Black BB.	Purplish-black.	Colourless.	Turns bluer.	Colourless.	Deep blue.	Blue-black.
Calcutta Black 3 B.	Little change.	Colourless.	Little change.	Blue-black.	No change.	Colourless.
Thiophenol Black BF extra.	No change.	......	Little bluer.	Dull blue.	No change.	....
Immedial Brilliant Black 5 BV.	No change.	Colourless.	No change.	Colourless.	No change.	....
Anthracene Blue-Black C.	Redder.	Colourless.	Paler and redder.	Colourless.	No change.	....
Katigen Black T 3 B and BFC extra.	No change.	Colourless.	No change.	Colourless.	No change.	....
Erio Chrome Blue-black B.	No change.	Colourless.	Black.	Blue.	No change.	Colourless.
Triazol Black B..	No change.	....	Greener.	Greenish-blue.	No change.	....
Naphthomelan SB.	No change.	....	No change.	....	No change.	

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Fibre and solution crimson.	Dull purple; on warming buff. Soln. colourless.	Suitable for printing wool. Does not gelatinise, or sublime on steaming.
....	....	Fbre and solution deep crimson.	Little change.	Direct cotton dye.
....	....	Fbre and solution dull crimson.	No change.	Direct cotton dye. Fast to lustring, and finishing.
....	....	After a time, deep dull crimson. Solution pale crimson.	Little change.	Acid mordant dye. Suitable for machine dyeing or for knitting yarns.
....	....	Deep orange brown. Soln. pale brown.	Deep blue on warming. Soln. pale blue.	Acid mordant. Suitable for fabrics containing cotton effects.
....	....	Purplish-brown. Solution pale dull purple.	On warming *wool* decolourised, *cotton* dark brown.	For a good black on unicn material.
....	....	Fibre and solution deep claret red.	On warming, pale bluish-green.	Acid dye. Suitable for wool in a strongly acid bath. Cotton effects remain unstained.
....	....	Little change. Solution pale dull purple.	On warming chocolate brown.	Developed direct cotton dye. Suitable for cotton materials.
....	....	Little change. Soln. dull purple tint.	Turns a little browner on warming.	Sulphide dye for cotton.
....	....	Little change. Soln. purple.	Pale olive on warming.	Sulphide dyestuff, good blue-black shade.
....	....	Pale brown. Soln. colourless.	Almost decolourised on warming.	Acid mordant. Good fastness.
....	....	Little change. Solution grey.	No change.	Sulphide dyestuff.
....	....	Olive-brown. Soln. brown.	Light blue on boiling. Solution blue.	Acid mordant.
....	....	Purple. Solution pale purple.	Decolourised on warming.	Direct cotton.
....	....	Greenish-grey. Solution grey.	On warming pale brown.	Cotton printing.

IV.—GREEN COLOURS.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Cœrulein...........	Duller.	Claret.	Duller.	Amber.	No action.	....
Resorcin Green.......	Yellow.	Red.	Brown.	Brown.	Darker.	Greenish.
Acid Green..........	Pale green.	....	Brown.	Yellow.	Decolour	....
Alkali Green.........	Olive.	Brown.	Dk. brown.	Dk. brown.	Decolour	....
Methyl Green.........	Yellow.	Yellow.	Bleached.	Colourless.	Decol-ourised.	....
Malachite Green......	Orange.	Orange.	Bleached.	Orange.	Decol-ourised.	....
Helvetia Green......	....	Yellow.	Decolour-ised.	....	Buff.	....
Aldehyde Green......	Yellow.	....	Orange.	....	Paler.	....
Vat Indigo and Old Fustic.	Paler.	Blue.	Paler.	Blue.	Green-blue.	Yellow.
Vat Indigo and lead chromate.	Blue.	Yellow.	Yellow-green.	....	Blue.	Yellow.
Indigo carmine and picric acid.	Blue, then much paler.	Blue.	As HCl.	Blue.	Decol-ourised.	Yellow.
Chrome Green........	No action.	....	No action.	....	No action.	....
Azine Green....... ..	Violet.	....	Brown.	....	Darker.	....
Azo Green..........	Brown.	Yellow.	Brown.	Yellow.	Yellower	....
Brilliant Green.......	Yellow.	Yellow.	Red.	Red.	Decol-ourised.	....
Diamond Green.......	Bluer.	Yellow.	Bluer.	Blue.	....	....
Dioxin..............	Dk. brown.	Brown.	Dk. green.	Black.	Dk. brown.	Red.
Alizarin Green SW....	Redder.	Pink.	Blue.	Blue.	Greener.	....
Fast Green..........	Amber.	....	Yellow.	....	Greener.	....
Guinea Green........	Yellow-ish.	....	Brown.	....	Decol-our.	....
Gambin.............	Olive.	Yellow.	Olive.	Brown.	No action.	....
Indoine Blue 2 B.	Green.	Yellow.	Dark green.	Green.	....	....
Light Green SF.......	Orange.	Yellow.	Orange.	Yellow.	Decolour	....
Light Green S........	Brown.	Brown.	Red-brown	Yellow.	Decolour	....
Naphthol Green......	Yellow.	Yellow.	Olive.	Drab.	Brighter	Olive.
Victoria Green.......	Orange.	....	Yellow.	Yellow.	Decol-our.	....

IV.—GREEN COLOURS.—(*Continued.*)

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
No action.	....	Brown.	Red.	
No action.	....	Brown.	Paler.	Ash contains Fe.
Decolour.	....	....	Decolourised.	
Decolour.	....	....	No change.	
Decolourised.	....	....	Decolourised.	Heated to 100°—violet (distinction from malachite green).
Decolourised.	....	....	Decolourised.	
Buff.	....	....	Decolourised.	
Paler.	....	Brown.	Decolourised.	
Blue.	Greenish.	....	Paler.	Boiling solution $Al_2(SO_4)_3$—yellow with green fluor.
No action.	....	....	Blue, then decolourised.	Ash contains Pb and Cr.
Decolourised.	Yellow.	....	Decolourised.	Cold water extracts picric acid.
No action.	....	....	No action.	$CaOCl_2$—yellow sol.
....	....	Brown.	Brighter.	
Decolour.	....	Yellow.	Yellower.	
Decolourised.	....	Orange.	Yellower.	
....	....	Red.	Brighter.	Ash contains Cr.
Dk. brown.	Brown.	....	....	Ash contains Fe.
Greener.	....	Brown.	Gray.	Ash contains Cr.
....	....	Yellow.	Lighter.	
Decolour.	....	Orange.		
No action.	....	Red.	No change.	Ash contains Fe.
Lighter.	....	Yellowish.		
Decolour.	....	Yellow.	Brighter.	
Decolour.	....	Orange.		
No action.	....	Orange.	Decolourised.	
Decolour.	....	Red.	No change.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Columbia Green...	Dark slate. Restored on dilution.	....	Dull violet.	Light green on dilution.	Little or no action.	....
Diamine Green G	Darker.	....	Violet. Green on dilution.	....	Darker.	Green.
Fast Light Green.	Yellow. Greenish-blue on dilution.	....	Yellow.	....	Bluer.	Blue.
Janus Green G...	Bluish-green. Blue on dilution.	....	Olive-green Blue on dilution.	....	Blue.	....
Eboli Green T....	Very dark. Lighter on dilution.	....	Reddish-blue.	Dirty green on dilution.	Darker.	....
Benzo Green BB.	Dark brown, Reddish-brown on dilution.	....	Darker. Light brown on dilution.	....	Dark olive.	....
Milling Green S..	Bluish-grey. Yellowish-green on dilution.	....	Dirty mauve.	....	Little change.	....
Acid Alizarin Direct Green G.	No change.	Colourless.	Darker.	Green.	No change.	Colourless.
Alizarin Brilliant Green G.	No change.	Colourless.	Yellowish-brown.	Dark green.	No change.	Colourless.
Sulphon Acid Green B.	Greener.	Greenish.	Greener.	Greenish.	Bluer.	Colourless.
Diamine Nitrazol Green GF.	Reddish-violet.	Reddish violet.	Reddish-brown.	Red.	No change.	Colourless.
Thiogene Olive Green GGN.	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.
Oxamine Green G.	Slate blue.	Colourless.	Reddish-blue.	Pale violet.	Duller.	....
Immedial Brilliant Green G extra.	A little darker.	Pale green.	No change.	Colourless.	Dark green.	Pale violet.
Naphtol Dark Green G.	Light green.	Green.	Light green.	Dark green.	Violet.	Violet.
Cyanole Green B.	Orange.	....	Yellow.	....	No change.	....
Brill. Benzo Green B.	No change.	....	Grey.	....	Light blue.	....
Benzo Dark Green 2 G.	Black.	....	Blackened	....	Black.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Little or no action.	....	Light brownish-red.	Decolurised.	Substanive colouring matter; may be dyed on cotton, wool or silk.
....	....	Brick red.	Decolourised.	Direct cotton colour. Mixed wool and cotton goods.
....	....	Yellow. Green on dilution.	Yellow.	Same by gaslight as by daylight, acid colouring matter.
....	....	Green. Green on dilution.	Decolourised.	Dyed on union lining.
....	....	Claret red. Colour destroyed on dilution.	Decolourised.	Wool, cotton or silk (reactions for cotton) can be discharged pure white with zinc dust.
....	....	Olive brown. Light olive on dilution.	Little change.	Dyestuff for wool. Fast to light and milling, without mordant in one bath.
....	....	Pink. Decolourised on dilution.	Decolourised.	Direct cotton green. For ½ silk and ½ wool dyeing suitable for padding purposes. Discharged white with tin or zinc.
....	....	Orange.	No change.	Acid dyeing Alizarin dyestuff.
....	....	Yellow.	Light green on boiling, solution colourless.	Level shades, fast against light.
....	....	Maroon.	Decolourised on boiling.	Wool dye, good penetration.
....	....	Reddish-violet.	Decolourised on boiling.	Direct cotton dye. Can be coupled with paranitraniline.
....	....	Brown.	Brown on boiling. Solution colourless.	Fast to most agents except chlorine. Sulphide dye for cotton.
....	....	Purple.	Pale dull purple on warming.	Direct cotton, suitable for union dyeing.
....	....	Dark magenta.	Pale yellow on boiling. Solution colourless.	Sulphide dyestuff.
....	....	Red.	Decolourised on boiling.	Acid dye for wool.
....	....	Olive.	Pale yellow.	Acid dyestuff.
....	....	Olive.	Purple.	Direct cotton.
....	....	Dark violet.	Black, then blue, finally decolourised.	Direct cotton, all fibres.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Alizarin Dark Green W.	Slightly lighter.	....	Much greyer.	....	Lighter and bluer.	....
Diamined Dark Green N.	No change.	....	Black.	....	No effect.	....
Wool Green BS..	Greener.	....	Yellow.	....	Blue.	....
Chrome Green G..	No change.	....	No change.	....	Pale olive.	Deep olive.
Algole Dark Green B.	Olive.	Olive.	No change.	Colourless.	No change.	Colourless.
Kiton Green N.	Gradually to yellow.	Pale yellow.	Slowly decolourised.	Colourless.	No change.	....
Eclipse Green G..	Lighter.	Green.	Blue.	Violet.	Bluish-green.	Unchanged.
Alizarin Green G..	Crimson.	Orange.	Brown.	Yellow.	Lighter.	Yellowish-green.
Neptune Green SG	Yellow.	Colourless.	Yellow.	Yellow.	Colourless.	Colourless.
Thional Green 2 G.	Dull reddish-blue.	Colourless.	Bright reddish-blue then black.	Pale olive.	No change.	....
Anthraquinone Green GXN.	No change.	Colourless.	Dark green.	Green.	No change.	Colourless.
Pyrogene Dark Green 3 B	Turns bluer.	Colourless.	Bright sky blue.	Bright sky blue.	No change.	....
Pyrogene Green 3 G.	Turns bluer.	Colourless.	Reddish-blue.	Reddish-blue.	No change.	....
Guinea Fast Green B.	Bright yellowish-green then bright yellow.	Colourless.	Bright yellowish-green, then dull yellow.	Colourless.	No change.	....
Sulphur Green G extra.	Deep dull blue.	Colourless.	Deep dull blue.	Pale blue.	No change.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Olive brown.	Dark olive brown.	Mordant dye.
....	....	Purple.	Decolourised on warming.	Direct cotton.
....	....	Yellow. Original colour restored on washing (same as H_2SO_4).	Greener.	Acid green.
....	....	Brown.	Pale brown solution.	Mordant dye.
....	....	Yellower. Soln. colourless.	Maroon on boiling. Solution colourless.	Vat dye. Fast against washing, etc.
....	....	Yellowish-green then pale yellow; soln. pale yellow.	Changes to green.	Acid dye.
....	....	Decolourised. Solution pink.	Decolourised. Solution colourless.	Sulphur colour.
....	....	Yellow. Solution yellow.	On warming, brown. Solution pale red.	Acid mordant dye.
....	....	Yellow. Solution colourless.	Little change. Solution colourless.	Acid colour.
....	....	Fibre and solution bright purple.	Pale olive on warming. Solution colourless.	Sulphide dye. Fast to cross-dyeing, light, etc. Suitable for piece goods, machine dyeing, etc.
....	....	Light orange. Soln. colourless.	On boiling no change. Solution colourless.	Suitable for dyeing loose wool and yarn.
....	....	Fibre and solution purple.	Pale bluish-green on warming.	A sulphide dye. Fast to milling, acids, etc.
....	....	Fibre and solution bright reddish-violet.	On warming colour is greatly reduced.	A sulphide dye for cotton. It is fast to light, cross-dyeing, etc.
....	....	Golden yellow. Soln. pale yellow.	On warning, bright yellowish-green.	Acid dyestuff with easily leveling properties. Fast to light, washing, alkalies, stoving, etc.
....	....	Deep dull crimson. Soln. bright bluish-crimson.	On warming, almost decolourised.	Sulphide dyestuff, very soluble suitable for dyeing in machines. Fast to acids, milling, etc.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Thional Brilliant Green GX.	Turns bluer.	Colourless.	Reddish-blue.	Reddish blue.	No change.	....
Immedial Green GG extra.	Turns bluer.	Colourless.	Black.	Bluish-grey.	Turns bluer.	Colourless.
Erio-Viridine B...	Yellowish-green to golden-yellow.	Yellow tint.	Yellowish-green, then golden-yellow.	Pale yellow.	Pale green almost decolourised.	Colourless.
Para Green G....	Navy blue.	Colourless.	Violet-Blue.	Violet-blue.	Dull olive.	Colourless.
Fast Acid Green BB extra.	Orange-yellow.	Pale yellow.	Dull orange-yellow.	Colourless.	Sky blue.	Colourless.
Immedial Deep Green G.	Slate blue.	Colourless.	Reddish-blue.	Reddish-blue.	Yellower	Colourless.

V. YELLOW COLOURS.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Picric Acid..........	Decolour.	Yellow.	Decolour.	....	Orange.	Yellow.
Victoria Yellow......	Decolourised.	....	....	....	....	....
Naphthol Yellow.....	Decolourised.	Colourless.	Decolourised.	....	Orange.	Yellow.
Naphthol Yellow S...	Decolourised.	Colourless.	Decolourised.	....	Paler.	Yellow.
Aurantia............	Paler.	....	Drab.	....	No action.	....
Quinoline Yellow....	Yellow.	Colourless.	Yellow.	Colourless.	Decolourised.	....
Chrysoidine Yellow ..	Red.	....	....	Yellow.	Paler.	....
Fast Yellow..........	Red.	....	Brown.	....	No action.	....
Orange II...........	Violet.	Violet.	Violet.	Violet.	Deep red	....
Orange III..........	Red.	Pink.	Violet.	Violet.	Yellowish.	....
Orange IV...........	Violet.	Violet.	Violet.	Violet.	No action.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Purple. Soln. colourless.	On warming, olive-yellow.	A sulphide colour for cotton.
....	....	Bluish-purple. Soln. pale purple.	On warming, pale yellowish-green.	Sulphide dyestuff. Fast to light, washing and acids.
....	....	Orange. Solution deep yellow.	On warming, bluish-green.	Acid dye for wool. Cotton effects remain white.
....	....	Reddish-violet. Soln. colourless.	On warming, dull chocolate.	Direct dyeing colour. Develops a green colour with diazotised paranitraniline. Discharged with rongalite C.
....	....	Golden-yellow, soln. pale yellow.	On warming, yellowish-green.	Level dyeing acid dyestuff. Suitable for fancy shades on wollen piece goods and yarns.
....	....	Bluish-purple Soln. colourless.	Decolourised on warming.	New sulphide dye.

V. YELLOW COLOURS.—*Continued.*

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Paler.	Yellow.	....	Decolourised.	KCN—red.
No change.	....	....	....	Warm water extracts the colour.
Paler.	Yellow.	....	Decolourised.	KCN—red. Stains paper at 120°.
No change.	Yellow.	....	Bleached.	
No action.	....	....	Brown.	
No action.	....	Deep yellow.	No change.	
Yellower.	....	....	Decolourised.	
No action.	....	Red.	Decolourised.	
No action.	....	....	Decolourised.	
No change.	Yellow.	....	Decolourised.	
No change.	Yellow.	....	Decolourised.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Citronin.............	Violet.	Violet.	Violet.	Violet.	Green-yellow.	Colourless.
Crocein Orange......	Brown.	Pink.	Darker.	Orange.	Brown.	....
Chrysamin...........	Brown.	Pink.	Magenta.	Violet.	Dark orange.	Colourless.
Hessian Yellow......	Black.	Violet.	Dark violet.	Violet.	Dark red.	Pink.
Brilliant Yellow....	Dark violet.	....	Black.	Violet.	Red.	Pink.
Chrysophenin........	Black.	Colourless.	Brown.	....	No change.	Yellowish.
Primuline yellow.....	No action.	....	Paler.	....	Brighter	Colourless.
Tolylene orange......	Violet.	Reddish.	Magenta.	Colourless.	Brighter	....
Tolylene orange..... R.	Paler.	Yellow.	Yellowish.	Yellow.	Redder.	Colourless.
Primuline orange....	Brown.	Brown.	Brown.	Dark red.	Dark brown.	....
Oriol................	Red.	Red.	Red.	Red.	Redder.	Colourless.
Auramine...........	Decolour	Colourless.	Decolour.	Colourless.	Decolour	Colourless.
Curcumin W.........	Black.	....	Black.	Violet.	Red.	Pink.
Phosphine...........	Decolourised.	Yellow.	....	Green-yellow.	Paler.	....
Tartrazin............	Orange.	Yellow.	Orange.	Yellow.	Orange.	Yellow.
Nitro alizarin........	Straw yellow.	Yellow.	Brownish.	Yellow.	Claret.	Colourless.
Galloflavin.....	Darker.	Yellow.	Darker.	Yellow.	Darker.	Yellow.
Madder.............	No action.	....	Red.	Red.	Purple.	Purple.
Quercitron bark.....	No change.	Yellow.	Yellow.	Yellow.	No change.	Yellow.
Flavin..............	Yellow.	Yellow.	Yellow.	Yellow.	Yellow.	Yellow.
Old fustic...........	Orange.	Orange.	Brown.	Brown.	No change.	....
Young fustic.........	No change.	Yellow.	Brown.	Brown.	Brown.	....
Weld...............	No change.	Yellow.	Bright yellow.	....	No change.	Yellow.
Persian berries.......	No change.	Yellow.	Brown.	Yellow.	No change.	Yellow.
Annatto.............	No change.	Red.	Blue.	Blue.	No action.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
No change.	Colourless.	Violet.	Decolourised.	....
No action.	....	Black.	Decolourised on boiling.	$CaOCl_2$—decolourised.
Bright orange.	Colourless.	Gray.	Decolourised.	....
Dark orange.	Orange.	Brown.	Decolourised.	....
Red.	Pink.	....	Decolourised.	....
No action.	....	Violet.	Decolourised.	....
No action.	....	....	Slight action.	....
No action.	....	Grey.	Decolourised.	....
No action.	....	Violet.	Decolourised.	....
No action.	....	Brown.	Decolourised.	
Orange.	....	Orange-red.	Decolourised.	Very fast to light.
Paler.	Colourless.	White.	Decolourised.	
Red.	Pink.	....	Decolourised.	
Paler.	....	....	Decolourised.	
Orange.	Yellow.	No action.	Decolourised.	
No action.	....	Yellow.	Deep yellow.	Ash contains Cr.
Darker.	Colourless.	....	No action.	Fe_2Cl_6—olive-green.
Brown.	....	....	No change.	Fe_2Cl_6—olive-brown.
No change.	Yellow.	Blue.	No change.	Fe_2Cl_6—olive.
No change.	Yellow.	Dark brown.	Brown-yellow.	Fe_2Cl_6—olive.
No change.	Yellow.	Pale yellow.	Orange.	Fe_2Cl_6—olive.
Brown.	....	Dark brown.	No action.	Fe_2Cl_6—olive.
No action.	....	No action.	No change.	Fe_2Cl_6—olive.
....	Pale yellow.	Brown.	Brown.	Fe_2Cl_6—olive.
No action.	....	....	Decolourised.	$K_3Fe(CN)_6$—blue.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Turmeric	Brown.	Colourless.	Brown.	Brown.	Brown.	Brown.
Iron Buff	Decolour	....	No action.	....	No action.	....
Chrome Yellow	Decolourised.	Yellow.	Duller.	....	Redder.	Yellow.
Azo Flavin	Violet.	Crimson.	Violet.	....	Greener.	....
Uranin G	Brighter	Yellow.	Greener.	Yellow.	Orange.	Yellow.
Alizarin Yellow A	No change.	....	Dull yellow.	Pale yellow.	Darker.	....
Anthracene Yellow	Dark purple.	....	Maroon.	Maroon.	Darker.	....
Diamond Yellow G	Orange.	Yellow.	Red.	....	Darker.	....
Flavazol	Crimson.	Yellow.	Scarlet.	Orange.	No change.	....
Patent Fustin	Bright red.	Yellow.	Bright red.	Red.	Brown.	Brown.
Thioflavine T	Decolourised.	....	Brown.	....	Decolourised.	....
Milling Yellow O	Crimson	Crimson.	Crimson.	Red.	....	....
Yellow N	Violet.	Violet.	Dull green.	Violet.	....	....
Tropæolin OO	Violet.	Violet.	Violet.	Violet.	Brighter	....
Metanil Yellow	Purple.	Purple.	Dark purple.	....	Brighter	....
Orange G	Scarlet.	Pink.	Crimson.	Red.	Terra-cotta.	....
Orange GT	Red.	Pink.	Crimson.	Crimson.	Darker.	
Orange R	Scarlet.	Pink.	Crimson.	Red.	Terra-cotta.	....
Alizarin Orange W	Lighter.	Yellow.	Darker.	Brown.	Redder.	....
Alizarin Orange S	Yellow.	Yellow.	Darker.	Brown.	Redder.	....
Benzoflavine	Orange.	....	Lighter.	....	Lighter.	....
Benzo Orange R	Blue.	Colourless.	Blue.	Blue.	Crimson.	Colourless.
Cloth Orange	Violet.	....	Violet.	Violet.	Darker.	....
Chrysamin R	Violet.	....	Violet.	....	Pink.	....
Carbazol Yellow	Slate.	Colourless.	Blue.	Blue.	Orange.	Pink.
Clayton Yellow	Orange.	Colourless.	Brownish.	....	Scarlet.	Colourless.
Cotton Yellow G	Crimson	Colourless.	Red.	Red.	Orange.	Orange.
Curcumin S	Duller.	....	Brown.	....	Redder.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Brown.	Orange.	Yellow.	Brown.	Ash contains Al.
No action.	....	....	Decolourised.	H_2S—black.
No action.	....	....	Decolourised.	H_2S—black.
No change.	....	Red.	Lighter.	
Redder.	Yellow.	No change.	No change.	
Darker.	....	Greenish.	....	Ash contains Cr.
Darker.	....	Orange.	....	Ash contains Cr.
Darker.	....	Orange.	Brown.	Ash contains Cr.
No change.	....	Scarlet.	Scarlet.	
Brown.	Brown.	Red.	Terra-cotta.	
Lighter.	....	....	Brighter.	
Brighter.	....	Red.	Decolourised.	
Brighter.	....	Yellow.		
Brighter.	....	Red.	Darker.	
No change.	....	Red.	Brown.	
No change.	....	Yellow.	Decolourised.	
....	....	Yellow.		
Redder.	....	Yellow.	No change.	Ash contains Cr.
Redder.	....	Yellow.	....	Ash contains Cr.
Lighter.	....	....	Decolourised.	On cotton.
Scarlet.	Colourless.	Brown.	Decolourised.	On cotton.
Darker.	Pink.	Red.		
Orange.	....	....	Decolourised.	On cotton.
Redder.	Colourless.	Crimson.	Decolourised.	On cotton.
Orange.	Colourless.	Decolour.	Orange.	On cotton.
No change.	....	Crimson.	Decolourised.	On cotton.
Redder.	....	....	Decolourised.	On cotton.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Cresotin Yellow G	Violet.	Colourless.	Violet.	Violet.	Red.	Pink.
Congo Orange	Violet.	....	Blue.	Blue.	No change.	....
Thioflavine T	Decol-ourised.	....	Olive-green.	....	Darker.	....
Thioflavine S	Lighter.	Yellow.	Red.	Colourless.	No change.	....
Thiazol Yellow	Orange.	....	Brown.	Colourless.	Scarlet.	Colourless.
Mimosa	Orange.	....	Dark yellow.	....	Red.	....
Diamine Yellow N.	Violet.	....	Violet.	Violet.	Orange.	Pink.
Mikado Orange 4 R.	Olive.	....	Blue.	....	No change.	....
Mikado Orange R.	Olive.	....	Gray.	....	No change.	....
Nitrazine Yellow	....	Yellow.	....	Yellow.	....	Yellow.
Poppy 2 G	Red.	Red.	Deep red.	Scarlet.	....	Red.
Acridine Orange	Red.	Red.	Decolour-ised.	Colourless.	Bright yellow.	Yellow.
Oxyphenine	No change.	Yellow.	Red.	Brown.	No action.	....
Aurotin	Decol-our.	Colourless.	Brown.	Colourless.	Redder.	Yellow.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Alizarin yellow paste.	Brick-red.	Yellow.	Deep red-dish-yel-low. On dilution, fawn.	Drab.	Duller.	Yellow.
Curcuphenin	Brown.	....	Crimson. Yellow on dilution.	....	Orange.	....
Chlorophenin Orange R.	Brown.	....	Violet. Brown-orange on dilution.	....	Red-orange.	....
Crumpsall Yellow YYFD.	Dark red.	Orange.	Orange-red.	....	....	Yellow.
Direct Yellow R.	Greener. Original col-our restored on dilution.	....	Red.	....	Slightly redder.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Orange.	Colourless.	Violet.	Decolourised.	On cotton.
No change.	....	Crimson.	Decolourised.	On cotton.
Lighter.	....	....	Decolourised.	On cotton.
No change.	....	Brown.	Orange.	On cotton.
Orange.	Colourless.	Lighter.	Orange.	On cotton.
Orange.	....	....	Decolourised.	On cotton.
Orange.	Colourless.	Violet.	Decolourised.	On cotton.
No change.	....	Slate.	Decolourised.	On cotton.
No change.	....	Olive.	Decolourised.	On cotton.
....	Yellow.	....	Decolourised.	
....	Red.	Red.	Decolourised.	
....	Yellow.	Brighter.	Purple.	
No action.	....	No change.	Decolourised.	On cotton.
....	Yellow.	Lighter.	Decolourised.	

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Red.	Brick-red.	Mordant colour. For wool dyeing, wool or calico printing. Reactions are for wool with chromium mordant.
....	....	Pale olive.	Dark olive.	Direct dyeing colour. Cotton, wool or silk (reactions on cotton).
....	....	Olive.	Grey.	Direct dyeing colour. Cotton, wool or silk.
....	....	Orange.	Decolourised.	Calico printing and fast wool dyeing. Mixes well with alizarins.
....	....	Almost decolourised.	Almost decolourised.	Substantive, very soluble in water. Unsuitable for wool and all animal fibres.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Oxydiamine Orange G.	Dark violet. Brown on dilution.	....	Bright crimson.	....	Redder.	....
Homophosphine G.	Orange-pink. Colour restored on dilution.	....	Greenish-yellow.	Pink on dilution.	Yellow.	....
Alkali Yellow R	Browner.	....	Red.	....	Red.	....
Alcali Orange G..	Redder.	....	Yellowish-brown.	....	Brown.	....
Stilbene Orange 4 R.	Dark olive.	....	Dark blue. Brownish-yellow on dilution.	....	Brighter	....
Indanthrene Orange RT.	Yellow.	Yellow,	Little change.	Yellow.	No change.	Colourless.
Algole Orange R..	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.
Cloth Yellow GH.	Red.	Colourless.	Brownish-yellow.	Light yellow.	Light orange.	Yellow.
Benzo Fast Yellow 4 GL extra.	Claret.	Colourless.	Maroon.	Maroon.	No change.	Colourless.
Thioxine Orange R.	No change.	Colourless.	Yellowish-brown.	Yellow-brown.	No change.	Colourless.
Thioxine Yellow G	Orange.	Colourless.	Brown.	Brown.	Slightly redder.	Colourless.
Triazol Yellow G.	Blue.	Colourless.	Bluish-purple.	Colourless.	No change.	....
Triazol Fast Yellow G.	No change.	Light yellow.	Brown.	Brown.	No change.	Light yellow.
Erio-chrome Yellow GR.	Red.	Yellow.	Yellowish-red.	Yellow.	Orange.	Colourless.
Pluto Orange G ..	Dark reddish-brown.	....	Brown, turning to dark crimson.	Almost decolourised on dilution.	Scarlet.	....
Rheonine A......	Orange.	....	Light yellow.	....	Yellower	....
Dianil Yellow 2 R.	No effect.	....	No effect.	....	Orange.	....

Ammonia		Spot with nitiric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Dull red. Colour destroyed on dilution.	Yellow.	Can be treated with coupling process.
....	....	Yellow. Fibre and soln. orange; yellow on dilution.	Bright scarlet.	Basic dyestuff suitable for dyeing cotton mordanted with tannin, or leather.
....	....	Paler.	Lighter.	Direct cotton dyeing colour. Reactions for cotton.
....	....	Yellow.	Light yellow.	Direct cotton dyeing.
....	....	Dark green.	Dull yellow.	Direct cotton colour. Also for silk and half wool goods (not wool alone).
....	....	Yellow.	Light yellow on boiling. Solution colourless.	Vat dyestuff for cotton.
....	....	No change.	No change on boiling. Solution colourless.	Vat dye for cotton. Fast against chlorine, washing, boiling, acid, akali and light.
....	....	Orange.	Decolourised on boiling.	Acid mordant dyestuff for wool.
....	....	Claret.	Little lighter on boiling. Solution colourless.	Direct cotton dye. Silk, half-silk, printing and discharge work.
....	....	Orange.	Orange on boiling. Solution colourless.	Sulphide dye for cotton.
....	....	Orange.	Orange on boiling. Solution colourless.	Sulphide dye for cotton.
....	....	Violet.	Decolourised on warming.	Direct cotton. Wool, silk, half-silk and union material also dyed.
....	....	No change.	No change on boiling. Solution light yellow.	Direct cotton, unions, half-silk, chip and straw.
....	....	Orange.	Decolourised on boiling.	Acid mordant giving fast shades on wool.
....	....	Little change.	Olive-brown then slowly decolourised.	Substantive. Cotton or silk.
....	....	Yellow solution.	No change.	Calico printing.
....	....	Lighter.	No effect.	Direct cotton.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Chloranisine Yellow GG.	Slightly lighter.	....	Salmon-pink.	....	No change.	....
Resoflavine Paste.	Much lighter.	....	Decolourised.	....	Bright red.	....
Fast Light Yellow G.	Yellowish-brown.	....	Yellowish-brown.	....	Colour extracted.	....
Stilbene Yellow 4 G.	No change.	....	Dirty yellow.	....	Deeper.	....
Domingo Chrome Yellow G.	Red. Original colour restored on washing.	....	Red, same as HCl.	....	Orange.	....
Eclipse Yellow 3 G.	Orange.	Colourless.	Orange.	Colourless.	No change.	....
Krogene Yellow R.	Slightly darker.	....	Brownish-yellow.	Yellow.	Darker.	Pale pink.
Flavanthrene R...	No action.	....	Slightly redder.	Colourless.	No action.	....
Chlorazol Fast Yellow B.	No change.	....	Scarlet.	Pale scarlet.	No change.	....
Pyrogene Yellow 3 R.	Yellowish-brown.	Colourless.	Turns duller.	Yellow. tint.	No change.	....
Thional Yellow R.	Orange-yellow.	Colourless.	No change.	Pale yellow.	Little redder.	Colourless.
Sulphon Yellow 5 G.	Orange-yellow.	Colourless.	Little change.	Lemon-yellow.	Orange yellow.	Colourless.
Diamine Fast Yellow M.	Greyish-olive.	Brownish tint.	Deep bluish-crimson.	Colourless.	No change.	....
Salicene Yellow D.	Crimson.	Colourless.	Crimson, then scarlet.	Orange.	No change.	....
Immedial Yellow GG.	Orange.	Colourless.	Duller and redder.	Pale yellow.	No change.	....
Pyrazine Yellow GG.	No change.	....	Redder.	Yellow.	No change.	....
Alizarin Yellow 5 G.	Bluish-crimson.	Colourless.	Bright red.	Orange-yellow.	No change.	....
Sulphine A.......	Light orange.	Orange.	Brown.	Brown.	No change.	Colourless.

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
		Much lighter.	Declourised slowly.	Direct cotton.
....	....	Decolourised.	Decolourised slowly.	Direct cotton.
....	....	Yellowish-orange.	No effect.	Acid yellow (wool).
....	....	No change.	No change.	Cotton yellow.
....	....	Same as H_2SO_4.	As sulphuric acid.	Mordant dyestuff.
....	....	Decolourised. Solution yellow.	No change.	A sulphur colour.
....	....	Redder. Solution orange.	On warming, yellowish-brown.	A sulphur colour.
....	....	Redder. Solution pale yellow.	Pale olive on boiling. Solution colourless.	Alizarin dyestuff of Indanthrene class. Soluble in alkaline hydrosulphite.
		No change Solution lemon yellow.	On warming, dull brown. Solution colourless.	Substantive cotton dyestuff. Fast to light, acids, alkalies, washing and bleaching.
....	....	.. Fibre and solution orange.	On warming, pale orange-yellow.	Sulphide dye. Fast to acids, milling, etc.
....	....	Orange-yellow. Soln. pale yellow.	On warming, orange-yellow.	Sulphide dye for cotton. Fast to milling, washing, etc.; without after treatment.
....		Little change. Soln. pale lemon-yellow	Turns redder on warming.	Suitable for dyeing wool in an acid bath. Fast to light and milling.
....	....	Purple. Solution yellow.	On warming, dull orange-brown.	Direct cotton dyestuff. Fast to chlorine. Suitable for dyeing 1/2 silk.
		Crimson then scarlet. Soln. orange tint.	Declourised on warming.	Acid mordant for wool.
....	....	Little change. Solution yellow.	Turns redder.	Sulphide dyestuff.
....	....	Paler. Solution yellow.	Decolourised on warming.	Acid dyestuff.
....	....	Fibre and solution scarlet.	Decolourised on warming.	Salicylic azo compound.
....	....	Light orange. Solution orange.	On boiling, light yellow. Solution yellow.	Dyes cotton direct. Orange shade only obtained on development

III. BLUE COLOURS.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Resorcin Blue	....	....	No change.	....	....	Blue, red fluor.
Benzoazurin G	Black.	Colourless.	Black.	Blue.	Dark red.	Pink.
Azo Blue	Black.	Colourless.	Black.	Blue.	Red.	Pink.
Soluble Blue	......	Blue.	Red-brown.	Red-brown.	Red-brown.	....
Spirit Blue	Green.	Brown.	Red-brown.	Red-brown.	Brick-red.	....
Alkali Blue 3 B	Blue.	Colourless.	Red-brown.	Red-brown.	Decolourised.	....
Victoria Blue	Black.	Red.	Black.	Orange.	Brown.	Colourless.
Indulines	Violet.	Blue.	....	Dark blue.	....	Violet decolour. by Zn dust.
Basle Blue	Grey.	Yellow.	Yellow.	Yellow.	Darker.	....
Indophenol Blue	Brown.	....	Brown.	....	No change.	....
Vat Indigo Blue	No change.	....	....	Blue.	No change.	....
Indigo Carmine	No change.	Bluish.	....	Violet.	Greenish.	Brown.
Logwood Blue	Red.	Red.	As HCl.	As HCl.	Purple.	Purple.
Prussian Blue	No action.	....	No action.	....	Brown.	....
Ultramarine Blue	Decolourised.	....	Decolourised.	....	No action.	....
New Blue	Purple.	....	Gray.	Gray.	Violet.	Pink.
Naphthalene Blue G	Violet.	Orange.	Black.	Brown.	Brown.	Orange.
Nile Blue	Yellow.	Yellow.	Red.	Red.	Red.	Pink.
Alizarin Blue	Violet.	Orange.	Violet with dilution.	Red with dilution.	Greenish.	....
Methylene Blue	Decolourised.	Blue-green.	Green.	Green.	Violet.	....
Alizarin Cyanin R	Redder.	Blue.	Violet.	Violet.	Greener.	....
Alizarin Indigo Blue	Darker.	Pink.	Darker.	Violet.	Greener.	Colourless.
Toluidine Blue	No change.	Blue.	Olive.	Greenish.	Crimson	....

III. BLUE COLOURS.—*Continued.*

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	Blue, red fluor.			
Dark violet.	Red.	....	Decolourised slowly.	Boiling soap solution—blue.
Dark violet.	Red.	....	Decolourised.	Picric acid—brown.
Decolourised.	....	Green.	Colour extract.	
Decolourised.	....	....	.. No change.	HNO_2—black spot.
Decolourised.	....	....	No change.	HNO_3—light green.
Green.	Colourless.	Brown.	Dark blue.	
....	As NaOH.	Dark green.	Violet solution.	Induline NN not changed by $CaOCl_2$.
No change.	....	Black.	No change.	
No change.	....	....	Decolourised.	Boiled with olive oil—colour extracted.
No change.	....	Yellow.	Paler; solution yellow.	Chloroform extracts colour.
As NaOH.	As NaOH.	Yellow.	Decolourised.	Boiling dil. Na_2CO_3—colour extracted.
Purple.	Purple.	....	Brown.	
No action.	....	Green.	No action.	Ash contains Fe.
No action.	....	....	Decolourised.	Blue ash.
Violet.	Pink.	....	Green, then decolourised.	
Violet.	Brown.	....	Decolourised.	HCl gas—brown.
Violet.	....	Green, yellow rim.	Decolourised.	
No action.	....	Yellow, turning brown.	Violet, red on heating.	Ash contains Cr.
No action.	....	Green.	Decolourised.	$CaOCl_2$—decolourised.
....	....	Green.	Redder.	
Greener.	....	Yellow, violet rim.		
....	....	Olive.	Decolourised.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Thiocarmin R........	Green.	Green.	Green.	Green.	Darker.	....
Alkali Blue 4 B......	Redder.	Light green.	Red.	Red.	Brown.	....
Cyanin B............	Yellow.	....	Yellow.	....	Olive.	....
Chrome Blue.........	Crimson	Pink.	Crimson.	Maroon.	....	....
Patent Blue..........	Amber.	Yellow.	Yellow.	....	Green.	Blue.
Pure Soluble Blue....	Brighter.	Light blue.	Red.	Red.	Red.	....
Neutral Blue.........	Orange.	Yellow.	Orange.	Yellow.	Lighter.	....
Victoria Blue B......	Red.	Red.	Red.	Red.	Maroon.	Colourless.
Indazine............	Darker.	Blue.	Dark green.	....	Redder.	....
Metaphenylene Blue..	....	Blue.	Grey.	....	Duller.	....
Indamine Blue B.....	Darker.	Blue.	Darker.	Blue.	Purple.	....
Indoin Blue..........	Green.	Slate.	Olive.	Olive.	Violet.	Pink.
Paraphenylene Blue...	Darker.	Blue.	Darker.	Blue.	Purple.	....
Benzo Black Blue....	Greener.	Colourless.	Green.	Blue.	Darker.	Colourless.
Night Blue..........	Red.	Red.	Red.	Red.	Brown.	....
Naphthylene Blue R.	Dark blue.	....	Dark blue.	....	Brown.	....
Diamine Blue BX....	Violet.	Colourless.	Green-blue.	Blue.	Violet.	Colourless.
Diamine Blue 3 R....	Darker.	Colourless.	Green-blue.	Blue.	Magenta.	Pink.
Benzoazurin.........	No change.	....	Green-blue.	Blue.	Crimson.	Pink.
Brilliant Azurin 5 G..	No change.	....	Blue-green.	Light green.	Violet.	Colourless.
Benzoazurin 3G......	Darker.	Colourless.	Green-blue.	Blue.	Violet.	Pink.
Diamine Blue 6 G....	No change.	....	Olive-grey.	....	Redder.	Colourless.
Benzo Black Blue G..	No change.	....	Green.	....	No change.	....
Sulphonazurin.......	Violet.	Colourless.	Violet.	Violet.	No change.	....
Bavarian Blue DSF..	....	Bluish.	Red.	Red.	Red.	Colourless.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks.
Fibre	Solution.			
Darker.	....	Green.	Greener.	
Decolourised.	Blue.	Green.		
Bright.	Pale blue.	Yellow.		
....	....	Yellow.	Greener.	
No change.	Colourless.	Yellow.	Yellow.	
Decolourised.	....	Green.	No change.	
Lavender.	....	Green.	Green.	
Violet.	Colourless.	Green.	Darker.	
....	....	Maroon.		
....	....	Green.		
....	....	Green.		
....	....	Green.	Greener.	
Violet.	....	Yellow.	Lighter.	
No change.	....	Red.	Decolourised.	
Grey.	....	Red.	Greener.	
Brown.	....	....	Decolourised.	
Violet.	Colourless.	Brown.	Decolourised.	On cotton.
Violet.	Pink.	Yellow.	Decolourised.	On cotton.
Violet.	Pink.	Brown.	Decolourised.	On cotton.
Violet.	Colourless.	Crimson.	Decolourised.	On cotton.
Violet.	Pink.	Orange.	Decolourised.	On cotton.
No change.	....	Yellow.	Violet.	On cotton.
No change.	....	Red.	Decolourised.	On cotton.
No change.	....	Yellow.	Decoloruised.	On cotton.
Decolourised.	Colourless.	Green.	Decolourised.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Soluton	Fibre	Solution
Wool Blue S.	Yellow.	Colourless.	Orange.	Orange.	Decolour.	....
Naphthyl Blue.	Redder.	....	Green.	....	Green-blue.	Colourless.
Capri Blue NO.	Violet.	Violet.	Dark green.	Green.	Green.	Colourless.
Gallamine Blue.	....	Violet.	....	Violet.	Darker.	....
Azophenine Blue R and G.	....	Blue.	....	Dark blue.	Violet.	....
Heligoland Blue B.	Redder.	....	Green-blue.	Violet.	Violet.	....
Ketone Blue B.	Yellow.	....	Yellow.	....	Green.	....
Diamine Sky Blue FF.	Darker.	....	Green.	Green.	Redder.	Violet.
Diamine New Blue G.	Violet.	....	Green.	....	Darker.	....
Diamine Brilliant Blue G.	Darker.	....	Green.	....	Violet.	Violet.
Brilliant Azurine. B.	No change.	....	Green.	....	....	Magenta.
Acid Alizarin Blue BB.	No change.	....	Violet.	....	Bluer.	....
Diaminogene extra.	No change.	....	Dull blue.	....	No change.	....
Alizarin Blue.	....	Blue.	Blue.	Blue.	Violet.	....
Diamine Dark Blue B.	Darker.	....	Violet.	....	....	Violet.
Diaminogene Blue G.	Greener.	....	....	Violet.	Redder.	....
Keton Blue 4 BN.	Yellow.	....	Yellow.	....	Olive.	....
Diamine Azo Blue R.	No change.	....	....	Blue.	Violet.	Red.
Brilliant Alizarin Cyanine 3 G.	Drab.	....	Brown.	....	Greener.	Blue.
Titan Ingrain Blue.	No change.	Pale green.	Green blue.	....	Violet.	Pink.
Titan Como SN.	No change.	....	Red.	....	Violet.	....
Anthracene Blue SWX.	....	Violet.	....	Blue.	Deeper.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Decolour.	....	Yellow.	Decolourised.	
Green blue.	Colourless.	Violet.	No action.	
No action.	....	Green.	Decolourised.	
....	Violet.	Orange.	Yellow.	
Redder.	....	Violet.	Lighter.	
Violet.	....	Orange.	Decolourised.	On cotton.
No change.	....	Yellow.	Green.	
Darker.	Blue.	Red violet.	Decolourised.	On cotton.
No change.	....	Violet.	Decolourised.	On cotton.
....	Violet.	Violet.	Decolourised.	On cotton.
....	Violet.	Red.	Decolourised.	On cotton.
Bluer.	....	Violet.		
....	....	Brown.	Violet.	On cotton, diaz. and developed.
....	....	Violet.	Dark green.	
....	....	Crimson.	Decolourised.	
....	....	Red.	Decolourised.	Diaz. and developed with betanaphthol.
....	....	Yellow.	Green.	
....	....	Crimson.	Violet.	Diaz. and developed.
....	....	Drab.	Yellow.	
....	....	Crimson.	Grey.	Diaz. and developed.
....	....	Green.	No change.	....
....	....	Brown.	Violet.	....

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Coomassie Navy blue R.	No change.	....	Green.	....	Violet.	....
Paramine Navy Blue 2 R.	Redder.	....	....	Blue.	....	Violet.
Paramine Blue B.	Redder.	....	....	Indigo Blue.	....	Violet.
Lanacyl Blue BB.	Maroon.	....	....	Green.	Red.	....
Lanacyl Navy Blue B.	No change.	....	....	Bluish-green.	....	Violet.
Brilliant Alizarin Cyanine 3 G.	Drab. Blue-violet on dilution.	....	Light brown. Blue on dilution.	....	Greener.	Light blue.
Paramine Indigo Blue.	Redder.	....	....	Greenish-blue. Bluish-violet on dilution.	Violet.	Bluish-red.
Diamine Deep Blue B.	Brighter.	....	Greenish-blue. Reddish-blue on dilution.	....	Darker and brighter.	....
Naphtindone BB...	Green. Blue on dilution.	....	Dirty olive. Violet on dilution.	....	Dark violet.	....
Janus Blue R	Bluish-green. Blue on dilution.	....	Olive-brown. Violet on dilution.	....	Blue.	....
New Patent Blue B.	Almost decolourised. Bright green on dilution.	....	Light olive yellow. Green on dilution.	....	Greener.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Crimson.	Decolourised.	
....	....	Crimson.	Decolourised.	
....	....	Crimson.	Decolourised.	
....	....	Crimson.	Decolourised.	
....	....	Crimson.	Pale green.	
....	....	Drab.	Yellow.	Dyes wool in an acid bath without chrome (reactions). Fast to light, etc.
....	....	Violet to crimson.	Slowly decolourised.	New colour for cotton. Easily discharged with Zn powder and soda bisulphite or tin crystals.
....	....	Red. Brownish on dilution.	Slowly decolourised.	New direct cotton colour. Easily dischargeable with tin crystals and Zn dust.
....	....	Bright green. Bluer on dilution.	Decolourised.	Blue basic dyestuff. Well adapted for printing all kinds of cotton or linen fabrics.
....	....	Yellowish-green. Green on dilution.	Decolourised.	Dyed on union lining.
....	....	Lemon-yellow.	Light yellow.	New wool dyestuff. Ladies' dress goods and fine yarns. Useful for dying silk, leather, feathers, paper and ink making.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Intensive Blue.....	Yellowish-brown. Dark blue on dilution.	....	Orange-brown. Bluish-violet on dilution.	Bluish-violet on dilution.	Slightly bluer.	....
Brilliant Cresyl Blue 2 B.	Dull-reddish-brown. Dark greenish-blue on dilution.	....	Dark green	....	Reddish-brown.	....
Lazuline Blue R....	Bright bluish-violet. Restored on dilution.	....	Bright green. Bright blue on dilution.	....	Reddish-blue.	....
Chlorazol Blue.....	Little change.	....	Darker and greener, gradually fading. Pink on dilution.	....	Purple.	....
Diazo Indigo Blue..	Darker. Redder on dilution.	....	Dark purple.	....	Darker.	....
Immedial Indogene BCL.	No change.	Colourless.	Bluish-violet.	Bluish-violet.	No change.	Colourless.
Immedial Direct Blue BB.	Bluish-violet.	Colourless.	Brown.	Violet.	Violet.	Colourless.
Diamine Bengal Blue G.	No change.	Colourless.	Violet.	Violet.	Violet.	Violet.
Oxamine Pure Blue 6 B.	Violet.	Colourless.	No change.	Colourless.	Bluer.	Colourless.
Brilliant Acid Blue FF.	Yellow.	Yellow.	Yellow.	Yellow.	Blue.	Light blue.
Alizarin Cyanol B...	Claret.	Claret.	Red.	Purplish-red.	Blue.	Bluish.
Oxy Chrome Blue B.	Bluer.	Colourless.	Maroon.	Greenish.	Violet.	Violet.
Thiogene Blue JL...	Blue.	Colourless.	Brown.	Brownish.	Light blue.	Light blue.
Victoria Navy Blue LH.	Red.	Reddish.	Brown.	Brownish.	Blue.	Bluish.
Alizarin Direct Blue EB.	Olivegreen.	Greenish-yellow.	No change.	Colourless.	Darker.	Blue.
Anthracyanine 3 GL.	Yellow.	Yellow.	Little change.	Yellow.	Little change.	Blue.

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
....	....	Dirty yellowish-olive. Yellow on dilution.	Dark green.	Homogeneous dyestuff for wool dyeing. Can be used for shoddy, and silk printing.
....	....	Orange. Greenish-yellow on dilution.	Decolourised.	Basic dyestuff. Dyed on mordanted cotton with tannic acid and tartar emetic.
....	....	Yellow.	No change.	Acid Colour.
....	....	Light brown. Decolourised on dilution.	Turns slowly to dull violet.	Belongs to a new group of colouring matters.
....	....	Dark red.	Greener. Then slowly decolourised.	Direct dyeing and diazotisable colour for cotton.
....	....	Violet.	Decolourised on boiling.	Sulphide dye. For all branches of cotton and for producing resist styles.
....	....	Violet.	Decolourised on boiling. Solution colourless.	Sulphide dye for cotton.
....	....	Reddish-brown.	Decolourised on boiling.	Direct cotton. For cotton and unions.
....	....	Violet.	Decolourised on boiling.	Direct cotton.
....	....	Yellow.	Yellow on boiling. Solution yellow.	Acid dyestuff. Loose wool, yarn and piece goods, etc. Exhausts well in Glauber's salt bath.
....	....	Brown.	Yellow on boiling. Solution yellowish.	Even dyeing bright blue. Fast against light.
....	....	Reddish-yellow.	Decolourised on boiling.	Acid mordant dye for wool.
....	....	Violet.	Decolourised on boiling.	Sulphide dye for cotton.
....	....	Green.	Green on boiling. Solution yellow.	Acid dye for dress material and woollen yarns.
....	....	Yellow.	Greenish-blue on boiling. Solution brown.	Acid dye. Fast against alkali, perspiration and light.
....	....	Yellow.	Becomes greener on boiling.	Acid dye. Dress goods, carpet yarns, etc.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Thiogene New Blue BL	Darker in shade.	Colourless.	Dark blue.	Dull blue.	Lighter in shade.	Blue.
Brilliant Fast Blue 2 G.	Paler and redder.	Colourless.	Greener.	Colourless.	A little redder.	Colourless.
Triazol Pure Blue R.	No change.	....	Bluish-green.	Colourless.	No change.	....
Acid Cyanine BD.	Darker.	Dark blue.	Much darker.	Violet.	Darker.	Violet.
Erio-Chrome Blue BR.	Bluer.	Light yellow.	No change.	Colourless.	Lighter.	Violet.
Indanthrene Blue RC.	No change.	Colourless.	Green.	Green.	No change.	Colourless.
Eboli Blue 2 R...	Dark purple.	....	Dark blue.	On dilution reddish-purple	Reddish-purple.	Bleeds a little.
Immedial Blue C.	No change.	....	....	Blue.	Little change.	....
Alizarine Sapphiroll SE.	Light green.	....	Olive.	....	Little change.	....
Dianil Dark Blue 3 R.	Reddish-blue.	....	Light blue.	....	Red.	....
Peri Wool Blue B.	Violet.	....	Violet.	....	Violet.	....
Oxamine Blue G..	Bluer.	....	Bluer.	....	No change.	....
Katigen Chrome Blue 6 G.	Violet.	....	Violet.	....	Blue.	....
Anthraquinone Blue SR.	Dark blue.	....	Violet.	....	No change.	....
Diamine Fast Blue C.	Redder.	....	Darker and greener.	....	Darker.	....
Cyanol AB.......	Green.	Colourless.	Colour destroyed.	....	Green.	Light green on heating.
Indigo JRG......	No change.	....	No change.	....	No change.	....
Erioglaucine A...	Bright orange.	....	Pale dull orange.	....	Slightly greener.	....
Naphtogene Blue 2 R.	No change.	....	No change.	....	Redder.	....
Indocyanine B...	Violet.	Purple.	Green.	Green.	No change.	Tinted red.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Violet.	Dull yellow on boiling. Solution colourless.	Sulphide dye for cotton.
....	....	Pale reddish-brown.	Pale bluish-red on warming.	Direct cotton. Very fast to light.
....	....	Pale orange-brown.	Little change on boiling.	One of the purest and brightest direct cotton blues.
....	....	Dark reddish-blue.	Reddish-brown on boiling. Solution red.	Acid dye for wool.
....	....	Brown.	Greenish-blue on boiling. Solution light yellow.	Acid mordant dye for wool.
....	....	Green.	No change on boiling.	Vat dyestuff for cotton.
....	....	Dirty red-brown.	Very slowly decolourised.	Substantive for all fibres.
....	....	Violet solution.	Dark brown.	Sulphide colour.
....	....	Fibre brown. Solution green.	Pale blue.	Acid colour (wool).
....	....	Brown.	Paler	Direct cotton. Cotton or wool.
....	....	Maroon.	Violet.	Acid dye for wool.
....	....	Dark red.	No change.	Direct-dyeing cotton blue.
....	....	Violet.	Blue.	Sulphide blue.
....	....	Brown.	When heated, first blue then greenish-grey.	New alizarin dye.
....	....	Decolourised.	Decolourised on heating.	Direct cotton.
....	....	Decolourised.	Bright yellow on heating.	Cheaper brand of cyanol, giving duller shades.
....	....	Yellow.	No change.	Artificial indigo containing *indigo red*.
....	....	Light yellow.	No change.	Acid colour.
....	....	Little redder.	Little lighter.	Direct cotton.
....	....	Dark brown. Soln. dark purple.	Violet. Soln. colourless.	Acid dye.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Immedial Indone R...	Purple.	Colourless.	Dark blue.	Blue.	Red-dish-blue.	Colour-less.
Cyananthrol R	Red.	Colour-less.	Violet.	Blue.	Little change.	Colour-less.
Azo Wool Blue B....	Bright red.	Rose.	Crimson.	Crimson.	Lighter.	Brown.
Formyl Blue B......	Yellow.	Pale yellow.	Dull orange.	Yellow.	Blue-grey.	Colour-less.
Acid Alizarin Dark Blue SN.	No action.	....	No action.	....	No action.	....
Sulphur Blue L extra.	Reddish-purple.	Colour-less.	Dark blue.	Blue.	No action.	....
Thiogene Dark Blue.	Purplish-brown.	Colour-less.	Blue.	Blue.	Little change.	Colour-less.
Triazol Blue R......	No change.	....	Green.	Green.	Slightly redder.	Colour-less.
Xylene Blue BS.....	Bright yellow.	Pale yellow.	Yellowish-orange.	Colour-less.	Little lighter.	Pale blue.
Pyrogene Indigo......	Un-changed.	Colour-less.	Blue.	Dark blue.	Un-changed	Colour-less.
Diaminogene Blue NA.	Darker.	Colour-less.	Nearly black.	Blue.	Darker.	Colour-less.
Acetylene Sky Blue.	No change.	....	Pale blue.	Bluish-green.	Decol-ourised.	Blue.
Diaminogene Sky Blue N.	Brighter blue.	Colourless.	Slate.	Colour-less.	No change.	....
Benzyl Blue S.......	Orange.	Yellow.	Yellow.	Yellow.	Grey.	Colour-less

Ammonia		Spot with nitric acid	Stannous chloride and hydro-chloric acid	Remarks
Fibre	Solution			
....	....	Reddish-purple. Red solution.	Decolourised.	Sulphur colour.
....	....	Yellow. Solution yellow.	Little change. Purple solution.	Easily soluble. Blue alizarin dyestuff.
....	....	Yellow. Solution yellow.	On warming, green. Solution colourless.	Acid dyestuff.
....	....	Lemon-yellow. Solution yellow.	On warming, blue-green. Solution yellowish green.	Acid dye.
....	....	Dark olive. Solution pale violet.	Blue. Solution pale violet.	Acid mordant.
....	....	Redder. Solution purple.	Purple. Solution colourless.	Sulphur dye.
....	....	Fibre and solution amethyst colour.	On boiling, decolourised to greenish-grey. Soln. colourless.	Sulphur dye. Fast to sizing, washing, light, etc.
....	....	Fibre and solution pale red tint.	No change on boiling.	Direct cotton dyestuff. Can be diazotised and developed, with naphthol giving bright indigo shade.
....	....	Yellow. Soln. pale yellow.	Bright green on warming.	Bright blue wool dye. White cotton effects remained unstained. Suitable for shading chrome colours.
....	....	Blue. Solution blue.	Yellowish-green on warming.	Sulphide dyestuff for cotton. Brighter and faster than vat indigo.
....	....	Purplish. Solution colourless.	Bluish-purple on boiling.	Diazotisable direct cotton. Suitable for dyeing warps.
....	....	Bleached. Solution red.	Decolourised on warming.	Direct cotton dyestuff. When dyed on union materials the vegetable fibres dye up much more than the animal fibres.
....	....	Pale red. Solution colourless.	Reddish-blue on warming.	Diazotisable direct cotton. Suitable for warp dyeing.
....	....	Yellow. Solution yellow.	Blue. Solution green on warming.	Dyes very level Strong colouring power. Stands hot pressing. Suitable for self shades or mixtures.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium dydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Navy Blue BW......	Crimson.	Pale red.	Greenish-blue.	Purple.	Dark maroon.	Colourless.
Victoria Pure Blue B.	Colour destroyed.	Colourless.	Colour destroyed.	Dull yellow.	Pale dull blue.	Colourless.
Acetylene Pure Blue..	No change.	....	No change.	Bright blue.	Violet.	Pale Violet.
Marinol Acid Blue R..	Nut brown.	Colourless then bright red.	Gradually to dull purple.	Colourless.	Bluish-green.	Pale bluish-green.
Titan Como TG..	No change.	....	Grey, then maroon.	Colourless.	Dull purple.	Colourless.
Palatine Chrome Blue B.	No change.	....	Dull blue.	Pale blue.	No change.	....
Melanthrene B.......	Little change.	Colourless.	Olive.	Colourless.	No change.	....
Diazo Marine Blue G.	Reddish-blue.	Colourless.	Deep bright blue.	Deep bright blue.	No change.	....
Indochromine R. R...	Pale bluish-green.	Colourless.	Bright yellowish-green.	Colourless.	No change.	....
Wool Fast Blue BL..	No change.	....	Bluish-green.	Pale green.	Bluish-crimson.	Colourless.
Sulphur Indigo B....	No change.	....	Much deeper.	Colourless.	No change.	....
Toluylene Dark Blue GN.	No change.	....	Little change.	Reddish-grey.	No change.	....
Immedial New Blue G.	Bluish-violet.	Colourless.	Dark violet-blue.	Colourless.	No change.	....
Anthracene Acid Blue 2 R.	Violet.	Purple.	Duller and redder.	Colourless.	No change.	....
Chlorazol Brilliant Blue 12 B.	Turns redder.	Colourless.	Dull greenish-black.	Pale grey.	Dull reddish-blue.	Colourless.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Yellowish-brown. Soln. orange.	Green on warming.	Suitable for dress goods. Strong covering power.
....	....	Pale yellow. Soln. pale yellow.	Colour destroyed. Solution colourless.	Basic dye. Giving a brighter shade than Victoria blue B.
....	....	Fibre and solution purple.	Nearly decolourised. Solution colourless.	Bright sky blue direct cotton dye. In 1/2 wool, the cotton is dyed stronger.
....	....	Gradually from bright red to yellow. Soln. pale yellow.	On boiling, bright blue. Solution pale dull yellow.	Easy level acid dye. Cotton and ramie remain white.
....	....	Bluish-green. Solution colourless.	On warming, a little paler. Soln. colourless.	Substantive cotton dye-stuff of exceptional brightness.
....	....	Fibre and solution pale olive.	On warming reddish-blue. Solution pale blue.	Acid mordant dye giving dark shades on wool.
....	....	Dull yellow. Solution colourless.	No change.	Alizarin dyestuff. Greyish-black paste insoluble in water.
....	....	Fibre and solution pale crimson.	On warming a little paler and bluer. Solution colourless.	Direct cotton dye. Capable of development with phenols or amines.
....	....	Bright yellowish-green. Soln. colourless.	On warming decolourised.	Dyestuff which is suitable for printing cotton.
....	....	Deep dull purple. Solution purple.	Little change.	Acid dye. Cotton effects remained unstained.
....	....	Deep dull reddish-blue. Soln. colourless.	On warming, Pale dull yellow.	Sulphide dyestuff. Fast to light, washing, etc.
....	....	Dark purplish-grey. Solution colourless.	On warming colour slightly reduced.	Direct cotton dyestuff. Capable of being diazotised and developed and can then be used for cross dyeing.
....	....	Dull bluish-purple. Soln. colourless.	On warming, dull lemon-yellow.	Sulphide dye for cotton.
....	....	Orange brown. Solution colourless.	On warming decolourised.	An acid mordant dyestuff. Can be applied as a mordant dye.
....	....	Darker and duller. Soln. pale blue.	No change.	Direct cotton dye. Bright sky blue on cotton materials. Does not become redder on fading.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Chrome Fast Blue FR.	Violet.	Colourless.	Deeper and redder.	Violet-blue.	Brighter and bluer.	Colourless.
Brilliant Alizarin Blue 3 R.	Dark slate.	Colourless.	Dull bluish-green.	Colourless.	No change.	....
Thioxine Indigo Blue B.	Dark blue.	Blue.	Dark blue.	Blue.	Violet.	Violet.
Thioxine Dark Blue B.	Dark blue.	Blue-	Dark blue.	Blue.	Violet.	Violet.
Thional Blue 2 B.	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.
Brilliant Anthrazurol G.	Salmon.	Faint yellow.	Salmon.	Faint yellow.	Little change.	Light blue.

II. VIOLET COLOURS.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Gallein..............	Brown-red.	Amber-yellow.	Like HCl.	Like HCl.	Paler.	....
Fast Violet...........	Dark blue.	Blue.	Black.	Blue.	Black.	Violet.
Azo-Violet...........	Black.	Colourless.	Black.	Green.	Crimson	Colourless.
Hessian Violet.	Dark blue.	Colourless.	Dark blue.	Black.	Redder.	Colourless.
Heliotrope...........	Black.	Blue.	Blue-black.	Blue.	Crimson.	Colourless.
Methyl Violet	Brown.	Amber.	Brown.	Amber.	Decol.	....
Phenyl Violet or Spirit Violet.	Dark green.	Brown.	Brown.	Brown.	Decol.	....
Benzyl Violet.......	Brown.	Amber.	Brown.	Amber.	Decol.	....
Acid Violet 7 B......	Green.	Amber.	Blackish.	Red.	Decol.	Colourless.
Perkin's Violet.......	No change.	Pink.	No change.	....	Blue.	....
Gallocyanin..........	Violet.	Violet.	Black.	Blue.	Black.	Violet.
Muscarin............	Black.	Blue.	Black.	Green.	Black.	Colourless.
Alizarin.............	Yellow.	Yellow.	Yellow.	Yellow.	Bluer.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Pale dull reddish-brown. Soln. colourless.	Decolourised on warming.	Suitable for discharging with hyraldite.
....	....	Olive-green then old gold. Soln. colourless.	Dull yellow on warming.	Especially suitable for dyeing fast shades on slubbing, loose wool, yarns, and piece goods.
....	....	Reddish-blue. Solution red.	Decolourised on boiling. Solution colourless.	Sulphide dye.
....	....	Red. Solution red.	Decolourised on boiling. Solution colourless.	Sulphide dye.
....	....	Dark blue. Solution light red.	Brown on boiling. Solution colourless.	Sulphide dye.
....	....	Olive.	Yellow on boiling. Solution yellow.	Easily levelling acid dyestuff.

II. VIOLET COLOURS.—*Continued.*

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Paler.	....	Yellow.	Crimson.	Ash contains Cr.
No change.	Violet.	Black.	Decolourised.	
Violet.	Magenta.	Red.	Decolourised.	Picric acid—black.
Redder.	Violet.	Blue rim.	Blue then decolourised.	
No change.	....	....	Decolourised.	Picric acid—dark brown.
Lilac.	....	....	Green.	
Decolourised.	....	Green.	Decolourised slowly.	
Lavender.	....	....	Green.	
Decolour.	Colourless.	Olive.	Green.	
No change.	....	No change.	Brown.	
Black.	Violet.	....	Grey.	
Blue.	Violet.	Black.	Grey.	
No change.	....	....	Yellow.	

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Acid Violet BB........	Yellow.	....	Yellow.	Yellow.	Decolour	....
Acid Violet 6 B......	Orange.	Yellow.	Orange.	Yellow.	Decolour	....
Acid Violet 4 BN.....	Yellow.	Yellow.	Yellow.	....	Decolour	....
Acid Violet 4 RS.....	Decol-ourised.	....	Yellow.	Yellow.	Decolour	....
Alkali Violet.........	Orange.	Yellow.	Orange.	Yellow.	Decolour	....
Azarin.............	....	....	Crimson.	Crimson.	....	....
Azo-mauve N........	Blue.	....	Blue.	....	Redder.	....
Fast Acid Violet 10 B.	Green.	....	Green.	....	....	....
Formyl Violet 4 BS.	Yellow.	Yellow.	Yellow.	Yellow.	Decolour	....
Chrome Violet.......	Crimson.	Pink.	Yellow.	Yellow.	Lighter.	....
Crystal Violet 6B....	Orange.	Yellow.	Orange.	Yellow.	Lighter.	Colourless.
Methyl Violet 6 B....	Orange.	Yellow.	Orange.	Yellow.	Lighter.	Colourless.
Ethyl Purple........	Orange.	Yellow.	Orange.	Yellow.	Bluer.	....
Regina Violet........	Grey.	Brown.	Brown.	Brown.	Decolour	....
Heliotrope 2 B......	Bluer.	Colourless.	Violet.	Violet.	Crimson.	Pink.
Diamine Violet N....	Blue.	Colourless.	Blue.	Blue.	Redder.	Colourless.
Congo Violet.........	Bluer.	....	Bluer.	Violet.	Red.	Colourless.
Naphthyl Violet......	Redder.	....	Green.	....	Grey.	....
Congo Corinth B.....	Blue.	Colourless.	Blue.	Colourless.	Red.	Colourless.
Red Violet 4 RS......	Redder.	Violet.	Dark red.	....	Decol-ourised.	Colourless.
Fast Bluish-Violet....	Blue.	Colourless.	Green.	Green.	Bluer.	Violet.
Victoria Violet.......	Redder.	Rose.	Bluer.	Violet.	Red.	Colourless.
Hofmann's Violets...	Yellow.	Colourless.	Yellow.	....	Decol-ourised.	....
Regina Purple.......	Brown.	Colourless.	Brown.	Colourless.	Decolour	....
Benzo Fast Heliotrope 2 RL.	Grey.	Yellow.	Pale blue.	Colourless.	Violet.	Colour-less.
Indanthrene Violet R extra.	No change.	Colour-less.	Little change.	Colour-less.	Redder.	Colour-less.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Decolour.	....	Yellow.	Bluer.	
Lighter.	....	..Yellow.	Green.	
Decolour.	....	Yellow.	Green.	
Decolour.	....	Yellow.	No change.	
Decolour.	....	Yellow.	Green.	
....	....	Brown.	Brighter.	
Redder.	....	....	Decolourised.	
....	Blue.	Green.		
Lighter.	....	Yellow.	Green.	
Lighter.	....	Yellow; red rim.		
Lighter.	Colourless.	Yellow.	Green.	
Lighter.	Colourless.	Yellow.	Blue.	
Bluer.	....	Yellow.	Green.	
Decolour.	....	Yellow.	Bluer.	
No change.	....	Orange.	Decolourised.	
Redder.	Colourless.	Brown.	Decolourised.	
Paler.	Red.	Brown.	Decolourised.	
No change.	....	Red.	Redder.	
Red.	Rose.	Blue.	Decolourised.	
Decolourised.	Colourless.	Dark red.	No change.	
Paler.	Violet.	Scarlet.	Decolourised.	
Red.	Colourless.	Orange.	Decolourised.	
Paler.	....	Yellow.	Yellow.	
Decolour.	Colourless.	Yellow.	Brown.	
....	....	Violet.	Decolourised on boiling. Solution colourless.	Bright direct cotton. Extremely fast to light.
....	....	No change.	Red on boiling. Solution colourless.	Vat dyestuff for cotton. Good fastness.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Ciba Violet B........	Decolourised.	Colourless.	Bluish-green.	Slightly blue.	Bluer.	Colourless.
Ciba Heliotrope B....	No change.	Colourless.	Dark brown.	Dark brown.	No change.	Colourless.
Ethyl Acid Violet.... S 4 B.	Bluish-red.	Red.	Bright red.	Red.	Orange.	Orange.
Oxy-chrome Vio-.... let R.	Crimson	Pale crimson.	Crimson.	Pale crimson.	Crimson.	Crimson.
Alizarin Cyanol .... Violet R.	No change.	Colourless.	Dark blue.	Dark blue.	Light in shade.	Blue.
Immedial Indone .... Violet B.	Violet.	Colourless.	Violet.	Violet.	No change.	Colourless.
Violanthrene C. D. ..	No change.	....	Grey.	Colourless.	No change.	....
Triazol Violet B..... N.	Dark blue.	Colourless.	Darker.	Colourless.	Dark violet.	Violet tint.
Erio Chrome Vio-.... let 3 B.	Maroon.	Pink.	Red.	Dark red.	Violet.	Pink.
Oxamine Violet......	No change.	....	Redder.	....	No change.	....
Benzo Fast Violet.... R.	Slightly redder.	....	Bright purplish-red.	....	Slightly lighter.	....
Chloranisine Vio-.... let R.	Blue.	....	Blue.	....	No change.	....
Columbia Violet .... R.	Violet.	....	Blue.	....	No change.	....
Alizarin Irisol R.....	Slightly darker.	....	Dark greenish-blue.	....	Bright blue in cold.	Blue on heating.
Anthraquinone ...... Violet.	No change.	....	Stripped.	....	No change.	....
Anthracene .... Chrome Violet B.	Claret.	Colourless.	Crimson.	Crimson.	Purple.	Colourless.
Azo Wool Violet.... 7 R.	Redder.	Colourless.	No change.	Pale violet.	No action.	....
Thiogene Rubine.... O.	Purplish-blue.	Colourless.	Bluish-purple.	Colourless.	No change.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Redder.	Decolourised on boiling. Solution colourless.	Vat dye of remarkable fastness.
....	....	Darker.	Decolourised on boiling.	Vat dyestuff. Great fastness.
....	....	Orange.	Decolourised on boiling.	Level dyeing acid colouring matter. Cotton effects remain unstained.
....	....	Crimson.	Decolourised on boiling.	Acid mordant for wool.
....	....	Yellow.	Lighter in shade on boiling. Solution colourless.	Wool dyestuff. Fast against light.
....	....	Stripped.	Decolourised on boiling.	Sulphide dye for cotton.
....	....	Paler.	On warming, turns redder.	Indanthrene dyestuff. Fast shades on cotton.
....	....	Red.	Violet on boiling. Solution colourless.	Direct cotton dyestuff.
....	....	Brown.	Maroon on boiling. Solution violet.	Acid mordant dyestuff for wool.
....	....	Much redder.	Slightly redder.	Direct cotton (wool).
....	....	Decolourised.	Almost decolourised.	Direct cotton.
....	....	Decolourised.	Decolourised.	Direct cotton.
....	....	Decolourised.	No change.	Direct cotton.
....	....	Decolourised.	Decolourised on heating.	Dyes unmordanted wool in an acid bath. Becomes redder in gaslight.
....	....	Bright red.	No change.	Dyes in an acid bath. An alizarine dyestuff.
....	....	Crimson. Soln. crimson.	Little change. Solution colourless.	Acid mordant.
....	....	Redder and finally yellow. Solution colourless.	Decolourised on boiling.	Acid dye.
....	....	Pale, dull crimson. Solution colourless.	Turns bluer on warming.	Sulphide dyestuff, giving shades on cotton which are fast to light, acid, milling, alkali, etc.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Guinea Fast Violet 10 B.	Green then golden-yellow.	Pale yellow.	Olive then dull yellow.	Colourless.	No change.	....
Thiogene Heliotrope O.	No change.	....	Deeper and duller.	Dull purple tint.	No change.	....
Direct Violet N......	Reddish-blue.	Colourless.	Deep blue.	Colourless.	Turns redder.	Colourless.
Rosanthrene Violet 5 R.	Bluish-purple.	Colourless.	Blue.	Colourless.	....	....

VI. BROWN COLOURS.

Catechu Brown......	No change.	Orange.	No change.	....	No change.	....
Bismarck Brown....	Reddish.	Red.	Reddish.	Red.	Yellower.	Colourless.
Phenyl Brown.......	Paler.	Brown.	....	....	Paler.	Purple.
Benzo Brown	Darker.	Purple.	Black.	Brown.	No action.	....
Fast Brown RG......	Violet.	Violet.	Violet.	Violet.	Crimson.	Red.
Naphthylamine Brown.	Yellow.	Orange.	....	....	....	....
Alizarin Brown......	Orange.	....	Orange.	....	Bluer.	Bluish.
Anthracene Brown...	Yellower	Yellow.	Redder.	Brown.	Black.	Grey.
Peachwood..........	Orange.	Orange.	Orange.	Yellow.	Purple.	Red.
Camwood............	Red.	Orange.	Red.	Orange.	Purple.	Purple.
Manganese Brown...	Decolourised.	....	No action.	....	No action.	....
Fast Brown.........	Maroon.	Pink.	Violet.	Violet.	Scarlet.	....
Fast Brown.........	Crimson.	Pink.	Bluer.	Blue.	Darker.	....
Fast Brown 3 B......	Violet.	Violet.	Blue.	Purple.	Crimson.	....
Acid Brown R......	Violet.	Violet.	Violet.	Violet.	Scarlet.	....
Acid Brown G.......	Darker.	Yellow.	Purple.	Purple.	Darker.	....
Benzo Brown B......	Darker.	Brown.	Purple.	....	No change.	....
Benzo Brown G......	Dark brown.	Light brown.	Darker.	Gray.	No change.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Olive then olive yellow. Soln. yellow tint.	Bluish-green on warming.	An acid dye for wool. It well retains its hue in artificial light. Cotton effects remain white.
....	....	Pale reddish-brown. Soln. pale brown.	No change.	A sulphide dye for cotton. Fast to light and washing.
....	....	Pale reddish-brown. Solution colourless.	Reddish-blue.	Direct cotton dyestuff.
....	....	Purple. Solution colourless.	....	Capable of being diazotised and developed with Naphthol. Direct cotton dyestuff.

VI. BROWN COLOURS.—*Continued.*

No change.	....	....	Paler.	Ash contains Cr.
No change.	Brown.	....	Decolourised.	Boiling water extracts colour.
Paler.	Red-brown.	....	Pink.	
No action.	....	....	Yellower.	
Crimson.	Red.	Black.	Decolourised.	
Yellow.	....	....	Purple.	
No change.	....	....	Orange.	
Grey.	Colourless.	Black.	Yellow.	
Purple.	Colourless.	....	Red.	
Purple.	Colourless.	....	Red.	On wool only.
No action.	....	....	Decolourised.	Ash contains Mn.
Yellower.	Brown.	Yellow.	Lighter.	
Darker.	....	Yellow.		
Crimson.	Pink.	Orange.	Bluer.	
Scarlet.	Pink.	Yellow.	Decolourised.	
Brighter.	Brown.	Yellow.	No change.	
No change.	Brown.	Darker.	Lighter.	On cotton.
No change.	Orange.	Darker.	Lighter.	On cotton.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Cloth Brown.........	Violet.	....	Violet.	Violet.	Darker.	....
Congo Brown R.......	Violet.	....	Violet.	....	Crimson.	....
Cotton Brown R......	No change.	Orange.	Crimson.	Crimson.	No change.	....
Congo Brown V......	Violet.	Colourless.	Violet.	Violet.	Crimson.	Pink.
Congo Brown NBR..	Violet.	Colourless.	Blue.	Blue.	Redder.	Colourless.
Cotton Brown A......	Darker.	Colourless.	Dark green.	....	No change.	....
Cotton Brown N......	Darker.	Brown.	Black.	Grey.	No change.	....
Congo Brown G......	Violet.	Colourless.	Violet.	Violet.	Crimson.	Crimson.
Dioxin..............	Darker.	Brown.	Green.	Green.	Dark green.	....
Diamine Brown V....	No change.	....	Purple.	Purple.	No change	Pink.
Gambin.............	No change.	....	Brown.	Brown.	Yellower.	Yellow.
Hessian Brown 2B....	Drab.	....	Violet.	....	No change.	....
Mikado Brown G.....	Buff.	Colourless.	Violet.	Violet.	No change.	....
Tolylene Brown.....	Darker.	Pink.	Violet.	Violet.	No change.	....
Thiocatechin........	Little change.	Faintly yellow.	Darker.	....	Darker	....
Cachou de Laval.....	Little change.	Faintly yellow.	Redder.	....	Little change.	....
Crumpsall Direct Fast Brown O.	Dull crimson.	....	Deep violet. Light brown on dil.	....	....	Brown.
Cross Dye Drab......	Little action.	....	....	Greyish.	Little change.	....
Diamine Catechin G..	....	Red.	Violet. Brown on dilution.	....	....	Light brown.
Dianol Black-Brown..	Dark violet.	....	Violet. Reddish-drab on dilution.	....	Dark red.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
Darker.	....	Red.	No change.	
Lighter.	....	....	Decolourised.	On cotton.
No change.	....	Brown.	Lighter.	On cotton.
Scarlet.	Pink.	Red.	Decolourised.	On cotton.
Redder.	Pink.	No change.	Lighter.	On cotton.
No change.	....	No change.	Decolourised.	On cotton.
No change.	Orange.	Darker.	Lighter.	On cotton.
Redder.	....	Violet.	Decolourised.	On cotton.
Dark green.	Red.	....	....	Ash contains Cr.
No change.	....	Violet.	Decolourised.	On cotton.
No change.	....	Yellow.	Redder.	Ash contains Cr.
No change.	....	....	Decolourised.	On cotton.
No change.	....	Olive.	Decolourised.	On cotton.
No change.	....	Brown.	Decolourised.	On cotton.
....	....	Darker.	Darker.	Cotton colour.
....	....	Little change.	Little change.	Cotton Colour.
....	....	Violet to brownish-red.	Decolourised.	Direct cotton colour. Wool may be dyed with Glauber's salt. Reactions, cotton.
....	....	Darker.	Browner.	Dyes cotton direct without the aid of a mordant. Stands cross-dyeing.
....	....	Crimson to brown.	Decolourised.	New diamine colour. Best applied to cotton. Easily discharged with tin crystals or zinc dust.
....	....	Brownish-red.	Quickly decolourised.	Dyes a shade somewhat similar to Cachou de Laval. (Reactions, cotton.)

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Dianol Olive	Dark dull violet.	....	Dull violet. Greyish-olive on dilution.	....	Brown.	....
Benzo Chrome Brown G.	Reddish-violet.	....	....	Dark bluish-violet. Decolourised on dilution.	Reddish-brown.	....
Benzo Nitrol Brown G.	Bronze.	Orange.	....	Reddish-brown. Yellow on dilution.	No change.	....
Janus Brown R	Dirty grey. Dark brown on dilution.	....	Bluish-violet. Dirty brown on dilution.	....	Crimson.	....
Diamine Nitrazol Brown RD.	Dark brown.	....	Dark reddish-brown.	....	Darker.	....
Alkali Red-Brown 2 R.	Browner	....	Reddish-blue.	....	Red.	....
Alkali Dark Brown G 109.	Dark reddish-purple.	....	Bright blue. Pink on dilution.	....	Redder.	....
Durophenin Brown V.	Dark olive.	....	Greyish-black.	....	Darker and slightly redder.	....
Dianol Black-Brown.	Darker.	....	Dark dull blue.	Reddish-brown on dilution.	Darker.	....
Thiophene Brown DB.	No change.	....	Darker.	....	Darker.	....
Thioxine Brown G.	No change.	Colourless.	Brown.	Brown.	No change.	Colourless.
Immedial Yellow-Olive 5 G.	Redder.	Colourless.	Brown.	Brown.	No change.	Colourless.
Monochrome Brown G.	No change.	Colourless.	Redder and lighter.	Maroon	Lighter in shade.	Brown.
Diamine Fast Brown G.	Green.	Pink.	Dark brown.	Pink.	Redder.	Colourless.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Crimson.	Slowly decolourised.	Direct cotton colour. (Reactions on cotton.)
....	....	Fibre become yellow.	Lavender. Decolourised on warming.	Direct dyeing cotton brown. Can be after-treated with chrome and Cu sulphate.
....	....	Light brown.	Drab brown. Light drab on continued boiling.	Direct dyeing brown. Dischargeable with tin crystals with difficulty. Zinc powder with bisulphite, better.
....	....	Orange. Orange-brown on dilution.	Reddish orange.	Dyed on union lining.
....	....	Dark brown.	Darker.	Dyed on cotton yarn. In cross dyeing unions in an acid bath, the wool is stained; but imperceptibly.
....	....	Yellowish-brown.	Light brownish yellow.	Direct dyeing cotton colour.
....	....	Brownish-red.	Light reddish purple.	Direct dyeing cotton colour.
....	....	Olive-brown.	Olive-green.	Direct cotton colour. Does not bleed.
....	....	Dull brownish-red. Yellow soln. on dilution.	Decolourised.	Direct dyeing brown. Remarkably fast after chroming, to washing.
....	....	Little change.	No change.	For vegetable fibres. Unaffected by acids, alkalies, or light.
....	....	Redder.	No change.	Sulphide dye for cotton.
....	....	Redder.	No change on boiling.	Sulphide dye. Fast to light, washing, acid, stoving, and hot pressing.
....	....	No change.	Declourised on boiling. Solution colourless.	Single bath mordant for wool.
....	....	Green.	Decolourised on boiling. Solution colourless.	Direct cotton. Fast against light, washing and chlorine.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Indanthrene Brown B.	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.
Oxy Chrome Brown V.	Lighter.	Reddish.	No change.	Colourless.	Red.	Red.
Alkali New Brown D..	Little change.	Colourless.	Brown.	Brown.	Little change.	Light brown.
Paramine Brown.....	No change.	....	No change.	....	No change.	....
Anthracene Chromate Brown E B.	Little lighter.	Pink.	No change.	Colourless.	No change.	Colourless.
Oxamine Brown 3 G..	Maroon.	Colourless.	Dark red.	Dark red.	Bright red.	Colourless.
Erio-chrome Crown R.	Maroon.	Colourless.	Maroon.	Maroon.	No change.	Colourless.
Pluto Orange and Benzo-nitrol developer.	Dark brown.	....	Dark purple.	Brownish on dilution.	Darker.	....
Pluto Brown.........	Darker.	....	Dark purple.	Brownish on dilution.	Darker.	
Katigene Yellow Brown GG.	....	Dark brown.	....	Yellow.	No change.	....
Kryogene Brown.....	Little change.	....	Dirty brown.	....	No action.	....
Dianil Brown 3 G....	Very little change.	....	Light brown.	....	Reddish-brown.	....
Acid Anthracene Brown R.	Red.	....	Red.	....	Colour extracted.	....
Immedial Brown B..	No effect.	....	Black.	....	No effect.	....
Oxydiamine Brown 9.	Black.	....	Black.	....	Browner.	....
Diamine Brown G....	Black. Restored on washing.	....	Black. Restored on washing.	....	As sulphuric acid.	....
Naphtamine Brown R 2 B.	No effect.	....	Much lighter.	....	No change.	....
Palatine Chrome Brown W.	Light brown.	....	Light brown.	Dark brown.	Colour bleeds off.	....
Sulphur Brown G....	Much browner.	....	Darker.	....	Little browner.	....

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	No change.	No change on boiling. Solution colourless.	A vat dye for cotton.
....	....	Red.	Light red on boiling. Solution colourless.	Acid mordant for wool.
....	....	Little change.	Decolourised on boiling. Solution colourless.	Direct cotton dyestuff.
....	....	Yellower.	No change on boiling.	Suitable for calico printing.
....	....	Much lighter.	Light red on boiling. Solution light red.	Single bath mordant dyestuff. Loose wool and yarn.
....	....	Brown.	Decolourised on boiling.	Direct cotton dyestuff.
....	....	Maroon.	Light brown on boiling.	Acid mordant for wool.
....	....	Dark red-brown.	Little change.	Cotton and silk.
....	....	Dark red-brown.	Little change.	Cotton colour.
....	....	Brown solution.	Little change.	Sulphide colour.
....	....	Dirty brown.	Light brown.	Direct cotton.
....	....	Slightly yellower.	Slightly redder.	Direct cotton (also wool).
....	....	Bright red.	Slowly decolourised.	Acid mordant.
....	....	No effect.	No effect.	Sulphide.
....	....	Black.	Black. Original colour restored on washing.	Direct cotton.
....	....	As sulphuric acid.	No change.	Direct cotton.
....	....	Decolourised.	No change.	Direct dyeing cotton.
....	....	As HCl.	No action.	Acid mordant.
....	....	Very much browner.	No change.	Sulphur dye.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Eclipse Brown B.....	No change.	....	Brown.	Brown.	Lighter.	Yellow.
Metachrome Brown B.	Redder.	Light reddish-brown.	Light brown.	Crimson.	No change.	....
Dianol Cotton Brown N.	Black.	Pale orange.	Purple.	Purple.	Reddish-brown.	Pink.
Acid Alizarin Brown BB.	Reddish-brown.	Colourless.	Red.	Rose.	No change.	....
Thiogene Brown. GC.	Little change.	Colourless.	Little change.	Brown.	No change.	....
Pyrogene Cutch R...	Darker.	Colourless.	Dark brown.	Pale brown.	Darker.	Colourless.
Pyrogene Brown 4 R.	Redder.	Colourless.	Brown.	Buff colour.	Yellowish-brown.	Colourless.
Pyrol Brown G......	Darker.	Colourless.	Yellow.	Yellow tint.	Darker.	Colourless.
Triazol Brown G OO.	Maroon.	Colourless.	Purple.	Purple.	Bright orange.	Colourless.
Pegu Brown G.......	Reddish-brown.	Colourless.	Deep purple.	Purple.	No change.	....
Immedial Bordeaux G.	Little paler and redder.	Colourless.	Black.	Dull purple.	Yellowish-brown.	Colourless.
Direet Dark Brown M.	Black-brown.	Colourless.	Deep violet.	Deep violet.	No change.	....
Direct Brown-Yellowish 3 GO.	Black-brown.	Colourless.	Deep violet.	Deep violet.	No change.	....
Immedial Dark Brown D.	No change.	....	Little change.	Yellowish-brown.	No change.	....
Pyrogene Orange O...	Turns redder.	Colourless.	Little change.	Dull yellow.	No change.	....

Ammonia: Fibre	Ammonia: Solution	Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
....	....	Decolourised. Soln. brown.	No change.	Sulphur colour.
....	....	Light brown. Soln. light red-brown.	Redder. Solution light reddish-brown.	Single bath mordant.
....	....	Orange. Soln. yellow.	On warming, grey. Solution colourless.	Direct cotton.
....	....	Brown. Solution pale brown.	Nearly decolourised (pale brown) on boiling.	Acid mordant.
....	....	Orange. Solution brown.	On boiling becomes redder. Solution colourless.	Sulphur dye. Fast to washing, light, etc. No after-treatment required.
....	....	Deep brown. Solution reddish-brown.	Darker on boiling. Solution colourless.	Sulphide dyestuff. Fast to light, washing, acids, etc.
		Lighter. Soln. pinkish.	Little change on heating.	Sulphide dye. Fast to acids' washing, light, etc.
....	....	Orange-yellow. Solution pale yellow.	A little redder on warming.	Sulphide dye. Fast to acids, washing, light, etc.
....	....	Crimson. Soln. crimson.	No change on warming.	Soluble direct cotton dye. 1/2 wool or 1/2 silk may be dyed a solid shade.
....	....	Dull red. Solution orange.	Olive. Soln. colourless.	Direct cotton dye.
....	....	Fibre and solution dull orange.	On warming, dull purple. Solution colourless.	Sulphide dye. Fast to light, washing and boiling, acids.
....	....	Deep reddish-brown then cherry-red. Solution colourless.	No change.	Direct cotton dye.
....	....	Fibre and solution crimson.	No change.	Direct cotton dye.
....	....	Little change. Soln. dull yellow.	Little change.	Sulphide dye. Suitable for producing dark browns which can be toned with basic dyes.
....	....	Reddish-brown. Soln. dull yellow.	Turns redder.	Sulphide dye. Fast to milling, boiling, acids, etc.

Dyestuff	Hydrochloric acid		Sulphuric acid		Sodium hydroxide	
	Fibre	Solution	Fibre	Solution	Fibre	Solution
Kryogene Brown.... RB.	No change.	....	No change.	....	Turns yellower.	Colourless.
Immedial Cutch ... BG.	Turns redder.	Colourless.	Dark purplish-brown.	Colourless.	No change.	Colourless.
Chrome Fast .... Brown A.	No change.	....	No change.	....	Turns yellower	Colourless.
Domingo Alizarin.... Brown B.	Turns bluer.	Colourless.	Brighter and bluer.	Bluish-purple.	Turns redder.	Colourless.
Direct Brown 5 G.....	Dull bluish-purple.	Colourless.	Deep blue.	Colourless.	Redder.	Colourless.
Indanthrene .... Copper R.	Yellow.	Colourless.	Little lighter.	Light red.	No change.	Colourless.
Thiogene Cate-...... chu R	No change.	....	No change.	....	Turns yellower.	Colourless.
Milling Orange R.....	Crimson.	Colourless.	Little change.	Golden-yellow.	Brownish-red.	Colourless.
Indanthrene .... Brown B.	No change.	Colourless.	No change.	Colourless.	No change.	Colourless.

Ammonia		Spot with nitric acid	Stannous chloride and hydrochloric acid	Remarks
Fibre	Solution			
....	....	Orange-brown. Solution colourless.	No change.	Sulphide dyestuff, brown shades on cotton, fast to washing, boiling, etc.
....	....	Deep dull orange-brown. Solution a brownish tint.	Little change.	Brown sulphide dyestuff. An after-treatment with metallic salts is not essential.
....	....	Turns yellower. Solution colourless.	On warming, a little paler and redder.	Acid mordant, suitable for dyeing woollen piece goods etc. Copper has little effect.
....	....	Orange-brown. Solution colourless.	On warming, paler and redder.	Acid mordant. Suitable for obtaining purplish-brown shades on wool, yarn, etc.
....	....	Reddish-purple. Soln. colourless.	Little or no change.	Direct cotton.
....	....	Yellow.	Yellow. Solution colourless.	Vat dyestuff for cotton. In paste form.
....	....	Turns yellower. Solution pale brown.	Pale reddish-brown on warming.	Sulphide dye for cotton.
....	....	Scarlet. Solution yellow.	Decolourised on warming,	Acid mordant dyestuff.
....	....	No change. Soln. colourless.	On boiling, no change. Soln. colourless.	Vat dye for cotton.

COLOURING MATTERS IN FOODS.

By ALBERT F. SEEKER, B. S.

Substances employed for colouring foods may be divided into 3 general classes: Pigments and lakes, vegetable and animal extracts, and coal-tar colours. The extent to which each is used is about in the reverse order named, pigments being employed only for special purposes, whereas coal-tar colours are found in almost all classes of food products.

Pigments and lakes are commonly employed in tinting cane sugar (ultramarine) and rice (Prussian blue, ultramarine), for polishing rice and dried pease (talc), for "facing" tea (talc, ultramarine, Prussian blue), for colouring coffee (chrome yellow), for colouring fish and meat preparations (oxide of iron pigments, cochineal lake, and other lakes derived from natural and coal-tar colours), and for colouring confectionery, in which a great variety of these colouring matters are likely to be found.

The details of the nature and composition of the many lakes and pigments now on the market should be sought in some work devoted to the subject (see Bersch, *Manufacture of Mineral and Lake Pigments*, 1901; Jennison, *Manufacture of Lake Pigments*, 1900) it being sufficient for purposes of food inspection to ascertain the metals in the pigments and the metallic bases and the dyes in the lakes.

Yellow Pigments found in foods are likely to be compounds of one or more of the following metals: Pb, Cr, Sb, Bi, Ba, Ca, Zn, Co, Fe, Al, Cd and Sn.[1]

Red Pigments—Fe, Pb, Cr, Co, Mg.

Blue Pigments—Fe (combined with cyanogen), Al (as ultramarine), Cu, Co, Sn.

Green Pigments—Cu, Cr, Co, Zn, Mn, Ba, Fe.

Violet Pigments—Mn, Sn, Cr, Cu, Al (as ultramarine violet).

[1] Compounds of Hg or As owing to their toxicity will rarely be found.

Brown Pigments—Mn, Cu, Cr, Co, Fe.

These pigments are frequently tinted with chalk, barytes, talc or kaolin. Powdered charcoal is occasionally found in spices and some times brick dust. Lamp black is used to deepen the color of chocolate coatings in confectionery.

In general, *pigments* may be detected by examining the ash of the suspected sample for the metals enumerated above, though in doing this it should be remembered that small amounts of Ca, Mg, Fe, Al and Mn occur naturally in most animal and vegetable products. Before drawing conclusions it is always advisable to estimate the metals quantitatively. A microscopical examination of the sample is often sufficient to detect added pigments.

The lakes consist of coal-tar dyes or natural colours of vegetable or animal origin which are fixed upon some base or combined in such a manner as to render them insoluble. Aluminum and tin lakes are generally employed in the case of cochineal and vegetable colours, aluminium, tin, calcium, barium, lead, zinc, and sometimes antimony for the acid coal-tar colours (page 117), while the basic colours (pages 116 and 118) are made to combine with tannin, tannin and tartar emetic, resin and fatty acids, or compounds of tin and phosphoric acid. Sometimes the shade of these lakes is modified by admixture of barytes, kaolin, zinc oxide, gypsum or some other pigment.

Berry (*U. S. Dept. Agr., Bur. Chem., Circular* 25) has enumerated some of the coal-tar dyes commonly found in lakes.

Red.—Magenta, rhodamins (B, G, S, 6G, 12G), safranins, ponceaus (3R, 4GBL, GL, GR, 4R), Fast Red O, eosins, phloxins, Rose Bengal and Alizarins.

Orange.—Mandarin (R, G) Brilliant Orange RG, Orange (II, O, R), Ponceau 4GBL.

Yellow.—Auramin, Thioflavin T, Naphthol Yellow S, Metanil Yellow, Quinolin Yellow and Tartrazin.

Brown.—Bismark Brown, Acid Brown B.

Green.—Acid Green D, Ethyl Green, Diamond Green, Cœruleïne.

Blue.—Nile Blue A, Victoria Blue, Naphthalin Blue, Methylene Blue B, Alkali Blue D, Neutral Blue, Diphenylamin Blue, Patent Blue BN, Erioglaucin Blues, Basle Blue, New Blue, Water Blue.

Violet.—Methyl Violet B, rhodamins, gallein.

The natural colours of vegetable and animal origin most often found in lakes are:

Yellow.—Turmeric, annatto, weld, fustic, Persian berry and buckthorn.

Red.—Cochineal, safflower and sandalwood.

Green.—Chlorophyll, Chinese green, and the calcium compounds of unripe persian berries and buckthorn.

Violet.—Alum compounds of alkanet and logwood and the calcium compound of archil.

Blue.—Indigo sulphonic acid.

The lakes may be detected by means of the microscope, their metallic constituents by an examination of the ash of the sample, and the colours by first decomposing the lake with a solution of tartaric, oxalic, or hydrochloric acid, and then fixing on wool or shaking out with amyl alcohol as described below.

Natural Colours of Vegetable and Animal Origin.

These were formerly extensively used to colour food products, but have now been largely replaced by the coal-tar colours. Berry (*U. S. Dept. Agri., Bur. Chem., Circular* 25) has compiled a comprehensive list of natural colours giving their sources and uses. (See also W. M. Gardner's section, pages 383 to 434.)

Alder bark: Source—*Alnus glutinosa.* Yellow.

Alkanet: Source—*Baphorhiza tinctoria* (*Alkanna tinctoria* Tausch.; *Anchusa tinctoria* L.). Used in colouring medicines, oils, pomades, wine, etc., red to crimson. Alkanna green has also been prepared from the root (*Jour. Soc. Chem. Ind.*, 1903, **22**, 512).

Aloes: Source—Cape aloe, *Aloe spicata; A. arborescens; A. lucida; A. succotrina; A. vera.* Yellow.

Al root; or Aich root, sooranjee (India), suranjee (India): Source—*Morinda citrifolia; M. tinctoria.* Alumina lake, yellow.

Annatto; or anotto, orlean, roucou, orenetto, attalo, terra orellana, achiote: Source—*Bixa orellana.* Used for colouring oils, butter, etc.

Archil; or orchil, orseille, oricello, orchilla: Source—*Rocella montagnei* (new); *R. fuciformis* (old); *R. tinctoria.* Also prepared from any lichens containing orcin or its derivatives, *i. e.*, variolaria, lecanoria, evernia, cladonia, ramalina, usnea. Appears in liquid, paste, and powder, the latter form being a sulphonated derivative. Dyes unmordanted wool in neutral, alkaline, and acid solutions, and should not be mistaken for coal-tar dyes, in the double dyeing test.

Asbarg; or gandhaki (Afghanistan): Source—*Delphinium zalil.* Yellow lakes prepared from the blossoms.

Bahia wood: Source—*Cæsalpinia brasiliensis.* Exported from Bahia. Sometimes called Brazil wood. See under Redwoods.

Barberry: Source—*Berberis vulgaris.* Yellow basic dye.

Barwood; or camwood, kambe wood, bois du cam: Source—*Baphia nitida.* From west coast of Africa and Jamaica. (See under Redwoods.)

Bastard hemp: Source—*Datisca cannabina.* Alkaline solutions yellow.

Bilberry; or whortleberry: Source—*Vaccinium membranaceum; V. myrtillus.* Blue to purple.

Box myrtle; or yangmoe, of China; kaiphal, of India: Source—*Myrica nagi* (*M. sapida* Wall. and *M. integrifolia* Roxb.); *M. rubra.* Alumina lake, brown orange.

Brazilwood; or Fernambourgwood, Pernambuco wood, fernambuck wood, bois de fernambouc, Rothholz: Source—*Guilandina crista; Caesalpinia braziliensis.* Chiefly from Brazil and Jamaica. See under Redwoods.

Brazilett wood; or Jamaica redwood, Bahama redwood: Source—

Buckthorn: Source—*Rhamnus cathartica.* Purple juice which when treated with alkali becomes green. Used in confectionery as sap green.

Buckwheat: Source—*Fagopyrum fagopyrum.* Yellow colour from leaves and stalk.

Buttercup: Source—*Ranunculus bulbosus* and other species. Yellow.

Cabbage: Source—*Brassica oleracea.* Contains cauline, probably identical with the cyanin of wine.

Camwood; or gaban wood, poa-gaban: Source—Closely allied to barwood. From African coast. See under Redwoods.

Capers: Source—*Capparis spinosa.* Yellow.

Caramel: Source—From sugar. Brown.

Carrot: Source—*Daucus carota.* Yellow.

Catechu: Source—*Acacia catechu; Ourouparia gambier.* Brown to red colours. Influenced by oxidation. Contains catechin.

Celery; or smallage: Source—*Apium graveolens.* Yellow green.

Chamomile (Ger.); or matricario: Source—*Matricaria chamomilla.* Alumina lake, yellow.

Chay root; or chè root, cherri vello, sayavee, imbural, turbuli: Source—*Oldenlandia umbellata.* Contains alizarin, purpurin, etc.

Chelidonine juice: Source—*Chelidonium majus.* Yellow.

Chica-red; or crajina, carajara: Source—*Arrabidaea chica* (*Bignonia chica* Humb. and Bonpl.). Vermilion red powder insoluble in water, alkaline solutions, orange to red.

Chinese green; or lokao: Source—*Rhamnus tinctoria; R. dahurica.* Only natural green dye other than chlorophyll.

Chinese yellow: Source—*Gardenia grandiflora.* Other Chinese yellows are Wongsky, Wougshy, Wongschy, Hoang-tchy, Hoang-teng, Hoang-Tschi, Hoang-pe-pi, and Ti-hoang.

Chrysamic acid: Source—Aloes. Action of nitric acid on aloes. Yellow in alcohol.

Chlorophyll: Green colour of plants.

Cochineal; or cochenille, coccionella: Source—*Coccus cacti* (dried bodies of the female insect). Contains carminic acid soluble in water with purple colour; lakes, red to purple; aluminum or tin lakes, cochineal carmine or coccerin.

Cotinin: Preparation from young fustic. Yellow.

Cranberry; or red bilberry: Source—*Vaccinium vitisidaea* L. Red.

Cudbear; or cudbeard, perseo: Source—*Lecanora tinctoria; Variolaria orcina.* Differs from archil in being in powder form and free from excess of ammonia.

Cyanin: Colouring matter from petals of flowers. Occurs in wine. Blue, turning pink with vegetable acids.

Dragon's blood (palm): Source—*Daemonorops draco.* Red resin.

Dragon's blood (Socotra): Source—*Dracaena cinnabari.* Red resin.

Dwarf elder: Source—*Sambucus ebulus.* Red.

Dyer's broom: Source—*Genista tinctoria.* Yellow.

Dyer's woodruff: Source—*Asperula tinctoria.* Contains colours similar to alizarin.

Elderberry: Source—*Sambucus canadensis; S. nigra; S. pubens.* Red.

Fairy cup; or blood cup: Source—*Chlorosplenium aeruginosum.* Calcium lake, green.

Flavin: Prepared from oak bark. Olive yellow to dark brown powder.

Forget-me-not: Source—*Myosotis palustris.* See Cyanin.

French purple: Prepared from archil by treatment with acid.

Fustic (old); or yellow Brazil wood, Holland yellow wood, murier des teinturiers, bois jaune, Gelbholz: Source—*Chlorophora tinctoria* (*Morus tinctoria* L.; *Maclura tinctoria* D. Don.). Contains morin and maclurin. Yellow.

Fustic (young); or bois jaune de Hongrie, du Tirol, Fisetholz, fustel; Source—*Cotinus cotinus* (*Rhus cotinus* L.). Contains fisitin. Yellow.

Galangal (Javan): Source—*Alpinia galanga*. Alkaline solutions yellow.

Galangal (Chinese): Source—*Alpinia officinarum*. Alkaline solutions yellow. Used in Russia for making "Nastoika," a liquor.

Gamboge: Source—*Garcinia hanburyi; G. morella*. Red resin. Lakes, yellow.

Garancin: Formerly prepared from madder. Of historical interest only.

Gentian: Source—*Gentiana lutea*. Alkaline solutions yellow.

Goa powder: Source—*Vouacapoua araroba* (*Andira araroba*) Aguiar. Contains chrysarobin and chrysophanic acid. Yellow.

Golden seal; or Canadian yellow root: Source—*Hydrastis canadensis*. Yellow basic dye.

Harmala red: Source—*Peganum harmala*. Basic colour insoluble in water; alkaline solutions red.

Heartsease; or pansy, lady's delight: Source—*Viola tricolor arvensis*. Yields quercetin. Yellow.

Hollyhock: Source—*Althaea rosea; Malva sylvestris; M. rotundifolia*. Solutions, violet red. Crimson with acids. Green with alkalies. Alumina lake, violet blue.

Horse chestnut: Lakes, yellow.

Indian yellow; or piuri, pioury, purree, purrea arabica, jaune indien. Prepared in India from the urine of cows fed on mango leaves and contains yellow colouring matters, free and in form of magnesium or calcium salts.

Indigo: Source—*Indigofera anil* and other varieties. Insoluble in water. Becomes soluble by treatment with sulphuric acid, forming sulpho salts. Indigo carmine (blue).

Jackwood; or jack fruit of Ceylon: Source—*Artocarpus integrifolia*. Alumina lake, yellow.

Kamala; or kameela, ramelas, rottlera: Source—*Echinus philippensis* (*Rottlera tinctoria* Roxb). Red powder.

Kermes berries; or portugal berries, poke berries, pigeon berries, scoke berries: Source—*Phytolacca americanæ* (*Phytolacca decandra* L.). Reddish.

Kermes; or false kermes berries, grains de kermes, vermillion vegetal:

Source—*Coccus ilicis* (dried bodies of the female insect). Solutions and lakes, blood red.

Kino: Source—*Pterocarpus marsupium; Butea frondosa, B. superba,* and varieties; *Eucalyptus corymbosa.* Red colour.

Lac-dye; or lac-lac: Source—*Coccus laccæ* (from the female insect). Colours similar to cochineal.

Lapacho; or taigu wood: Source—*Tecoma lapacho* and allied species. Yellow colour.

Lima wood; or Costa Rica redwood: Similar to St. Martha wood. (See under Redwoods.)

Liquorice: Source—*Glycyrrhiza glabra.* Brown.

Litmus; or tournesol: Source—*Rocella, Lecanoria, Variolaria.* Red and blue.

Logwood; or Campeachy wood, Blauholz: Source—*Hæmatoxylon campechianum.* The unfermented extract forms yellow solutions if neutral, and blood-red solutions with calcareous water. The unfermented solution contains chiefly a glucoside which upon fermentation yields hæmatoxylin, and the latter is easily oxidised to hæmateïn. Various coloured lakes are formed. Hæmatoxylin forms rose-red colour with alum and a black violet lake with iron alum. Hæmateïn forms bluish-violet with alkalies; reddish-purple with sodium carbonate; reddish-purple with ammonia; bluish-violet lake with ammoniacal copper sulphate; violet lake with ammoniacal tin chlorid; black with ammoniacal iron alum.

Lopez root: Source—*Toddalia aculeata.* Contains berberin. Yellow.

Lomatiol: Source—*Tricondylus ilicifolia; Tricondylus myricoides.* Yellow.

Madder: Source—*Rubia tinctorum.* Natural source of alizarin dyes.

Mang-koudur; or oungkoudon, song-kou-long, jong koutong: Source—*Morinda umbellata.* Lakes, yellow to red.

Marsh marigold: Source—*Caltha palustris.* Yellow.

Mountain wormwood; or Genepi des alpes: Source—*Artemisia absinthium.* Yellowish.

Munjeet: Source—*Rubia cordifolia.* Similar to madder.

Myrtle berry: Source—*Myrtus communis.* Bluish-red.

Nettle: Source—*Urtica* sp.

Nicaragua wood: Source—*Guilandina echinata.* Boughs or twigs used. (See redwoods.)

Onion: Source—*Allium cepa.* Alumina lake, yellow-brown.

Oregon grape root: Source—*Berberis aquifolium.* Yellow basic dye.

Panama crimson: Source—Vine called China.

Parsley: Source—*Apium petroselium.* Alumina lake, yellow.

Peachwood; or St. Martha wood, Martin wood, bois du sang: Source—*Guilandina echinata.* From the Sierra Nevada in Mexico. See under Redwoods.

Persian berries; or yellow berries, Kreutzbeeren, Avignon-Körner, granes de perse, graines jaune, graines d'Avignon (*Rhamnus infectoria*), French berries (*R. alaterna*), Spanish berries (*R. saxatilis*), Italian berries (*R. infectoria*), Hungarian berries (*R. cathartica*): Source—Species of Rhamnus as given above. Alum lake, bright yellow; iron lake, dark olive.

Poppy; or field red corn: Source—*Papaver rhoeas.* Red.

Poplar buds: Source—*Populus* sp. Alumina lake, yellow.

Prickly pear: Source—*Opuntia opuntia.* Red.

Privet berries: Source—*Ligustrum vulgare.* Bluish-red.

Purple heart: Source—*Copaiva pubiflora.* Alum lake, yellow.

Puriri: Source—*Vitex littoralis.* Alum lake, yellow.

Quercitron: Source—*Quercus velutina* and varieties. Yields quercetin, yellow.

Quebracho- Source—*Quebrachia lorentzii.* Yellow color.

Redwoods: See Brazil, Bahia, Peach, Nicaragua, Sapan, Lima, Braziletto, Bar, and Camwood. These woods yield on treatment various red to yellow-red coloured solutions, no two woods giving exactly the same shades, *i. e.*, Brazilin, probably occurring as a glucoside, forms Brazilein on oxidation and yields lakes similar to alizarin. Florence, Berlin, and Venetian lakes are lakes of the soluble redwoods.

Rhubarb: Source—*Rheum officinale.* Yields chrysophanic acid, yellow.

Rue: Source—*Ruta graveolens.* Alum lake, yellow.

Safflower; or dyer's saffron, carthame, safran bâtard, bastard saffron: Source—*Carthamus tinctorius.* Yellow color. Triturated with French chalk and dried, forms various bright red "rouges."

Saffron; or azafran (Afgh.): Source—*Crocus sativus.* Yellow.

Sage: Source—*Salvia officinalis.* Yellow.

Sandalwood; or santalwood, lignum santalum, red santalwood, Saunders wood, red sandalwood, red Sanders wood, bois de santal,

Sandelholz: Source—*Pterocarpus santalinus; P. indicus.* Contains santalin, a fine red powder easily soluble in alcohol and acetic acid with a blood-red colour. (See under Redwoods.)

Sapan wood; or sappan wood, Japan wood, bois du Japon, also called red sandalwood, santalwood, sumbawa wood: Source—*Caesalpinia sapan.* Probably identical with caliatur wood or cariatur wood. (See under Redwoods.)

Saw-wort: Source—*Serratula tinctoria.* Alumina lake, yellow.

Sepia: Source—*Sepia officinalis.* Dark-brown ink-like pigment.

Sorgo red; or durrha: Source—*Andropogon sorghum.* Lakes, crimson red.

Spanish trefoil: Source—*Trifolium* sp.

Spinach: Source—*Spinacia oleracea.* Yellow.

Stringy bark: Source—*Eucalyptus macrorhyncha.* Orange to yellow.

Sun dew: Source—*Drosera whittakerii.* Lakes red to brown.

Sumac (Cape); or pruim bast: Source—*Colpoon compressum.* Alum lake, yellow.

Sumac (Sicilian): Source—*Rhus coriaria.* Alum lake, olive yellow.

Tyrian purple: Source—Murex, purpura, buccinium, etc. (sea shells).

Tumeric; or curcuma, Indian saffron, terra merita, souchet, safran d'Inde: Source—*Curcuma longa; C. rotunda.* Yellow colour.

Ventilago, Madras-patana; or oural patti, pitti, lokandi, kanwait, etc.: Source—*Ventilago madraspatana.* Lakes, blue.

Virginia creeper: Source—*Parthenocissus quinquefolia.* Red colour.

Waifa; or hoai-hoa, Chinese yellow berries: Source—*Sophora japonica.* Alumina lake, yellow.

Wall flower: Source—*Cheiranthus cheiri.* Yellow lakes prepared from the blossoms.

Wall lichen: Source—*Parmelia parietina.* Yellow.

Waras: Source—*Moghania congesta* (*Flemingia congesta* Roxb.). Red resinous powder.

Weld; or wau, gaude, yellow weed, dyer's rocket: Source—*Reseda luteola.* Alumina lake, yellow.

Whitethorn; or blackthorn: Source—*Crataegus oxyacantha.* Yellow lakes from blossoms.

Woad; or pastel, waid: Source—*Isatis tinctoria; I. lusitanica.* Contains indigo.

Of the above-named natural colours those most commonly used are:

Alkanet, annatto, archil, caramel, chlorophyll, cochineal, cudbear, fustic, indigo (sulphonated), logwood, Persian berries, quercitron, safflower, saffron, santalwood, turmeric, and weld. With the exception of caramel and chlorophyll all of these have been fully described on pages 383 to 434. Caramel and chlorophyll will be treated separately (pages 636 and 639) and sulphonated indigo now properly belongs among the coal-tar dyes.

With the exception of the three last mentioned all the commonly occurring natural colours may be extracted from their aqueous or weakly alcoholic solutions by acidifying with hydrochloric acid and shaking in a separatory funnel with amyl alcohol. In treating a food product or an aqueous extract of it in this way it frequently happens that the amyl alcohol also takes up other substances besides colour, and in order to remove these the amyl alcohol layer is washed two or three times with water and then evaporated to dryness on a steam bath. The residue is dissolved in 50% alcohol, the solution filtered and then shaken with two separate portions of light boiling petroleum ether. On separating the alcohol layer, diluting with an equal volume of water rendered slightly acid with hydrochloric acid, and shaking with a fresh portion of amyl alcohol the colour usually passes into this in a reasonably pure condition. The final amyl-alcohol layer is washed once with water to remove most of the acid and evaporated to dryness on a steam bath, this operation being considerably hastened by the addition of some ethyl alcohol. The colour may be identified in this residue by the reactions given on page 637, by the characteristics indicated on pages 383 to 434, and by what follows.

To secure a solution of the colour from substances of a solid or a pasty consistency they should be macerated and shaken wtih 70% alcohol. After filtering, the solution is diluted with water, acidified, and extracted with amyl alcohol as given above.

Great care and discrimination should be employed in carrying out tests for the identification of natural colours, and it is advisable in all cases before drawing conclusions to compare the reactions of the unknown colour with those of a sample of known identity under the same conditions. Many fruits naturally contain colouring matters which pass into the amyl alcohol layer when shaken with that solvent in acid solution and their reactions should be studied in order to avoid mistaking them for added colours. Truchon and Martin-Claude (*J. pharm. chim.*, 1901, **13**, 174) and Tolman (*U. S. Dept. Agri.*, *Bur.*

Chem., *Bull.*, **107**, rev., 193) have observed the following behaviour of natural fruit colours:

EXTRACTION OF FRUIT COLOURS WITH AMYL ALCOHOL.

Fruit	Colouration of acid solution[1]		Colouration of ammoniacal solution		Addition of a drop of H_2SO_4 to dyed fabric
	Juice	Amyl-alcohol extract	Juice	Amyl-alcohol extract	
Early cherries	Red	Yellow	Green	Uncoloured.	Yellow.
Ripe cherries	Red	Uncoloured	Green	Uncoloured.	Yellow.
Early strawberries	Red	Rose	Green	Uncoloured.	Rose
Ripe strawberries	Red	Red	Green	Uncoloured.	Rose (tints silk a rose red).
Raspberries	Red	Red	Green	Uncoloured.	
Red currants	Red	Uncoloured	Green	Uncoloured.	
White currants	White	Uncoloured	Brown	Uncoloured.	
Black currants	Dark red.	Red	Deep green.	Uncoloured.	Tints silk rose.
Peaches	Yellow	Uncoloured	Brown	Yellow-red.	Uncoloured.
Pears	Yellow	Uncoloured	Brown	Yellow-red.	
Quinces	Yellow	Uncoloured	Brown	Yellow-red.	
Apples	Yellow	Uncoloured	Brown	Yellow-red.	
Apricots	Yellow	Uncoloured	Brown	Yellow-red.	
Green gage plums	Yellow	Uncoloured	Brown	Yellow-red.	

EXTRACTION OF FRUIT COLOURS WITH AMYL ALCOHOL AND WITH ETHER.

Fruit	Colour with ammonium hydroxide	Colour extracted by ether from acid solution	Colour extracted by amyl-alcohol from acid solution	Dyeing tests on the juice
Strawberry	Purple	None	Deep red	Colour washed out.
Red raspberry	Purple	None	Deep red	All colour does not wash out, but does not dye in the second acid bath.
Blackberry	Blue-purple	None	Very deep red	Dyes purplish-red in acid solution, but does not dye in the second acid bath.
Cherry	Purple	None	Red	Dyes purplish-red in acid solution, but does not dye in the second acid bath.
Blackberry	Blue-purple	None	Red	Dyes purplish-red in acid solution, but does not dye in the second acid bath.
Wild dewberry	Blue-purple	None	Red	Dyes purplish-red in acid solution, but does not dye in the second acid bath.
Currant	Blue-purple	None	Red	Dyes purplish-red in acid solution, but does not dye in the second acid bath.

The dyeing tests referred to in the second table were made with wool as described on page 642.

For the purpose of identifying the natural colours besides employing Leeds' scheme, Vol. II, page 308, and the general characteristics given

[1] Acidity of the juice.

REACTIONS OF VEGETABLE COLOURS ON WOOL, MORDANTED WITH TIN SALTS.

Colours produced by various reagents.

Colouring matter	Hydrochloric acid (sp. gr. 1.16)	Sulphuric acid sp. gr. 1.84)	Nitric acid	Stannous chloride, hydrochloric acid, and water	Sodium hydroxide 10 % solution	Boiling alcohol	Boiling soap (1% solution)	Boiling sodium carbonate (0.5 %) solution	Boiling 5% sulphuric acid solution
Logwood....	Red violet...	Olive-brown; yellow on dilution.	....	Red to violet	Violet......	No colour...	No colour...	No colour...	Red to orange-red.
Fustic	Yellow solution; colourless on dilution.	Solution yellow on dilution remains yellow.	Brown; on addition of sodium hydroxide, red.	Little action.	Browner; solution yellow, decolourised on adding hydrochloric acid.	No colour...	Solution deeper yellow; fibre straw colour.	As with soap.	Solution yellow: fibre not greatly affected.
Young fustic.	Solution yellow.	Fibre orange; solution yellow; colourless on dilution.	Fibre dark brown.	Solution faint yellow.	Yellow.				
Quercitron.	Yellow solution; colourless on dilution.	Yellow solution; yellow on dilution.	Orange-yellow; red with sodium hydroxide.	Little action.	Fibre browner; solution yellow.	No colour...	Solution faint yellow; fibre browner, but not much lighter.	Yellow solution; fibre brown-yellow.	Solution yellow; fibre not much affected.
Weld.......	Little affected.	Yellowish-olive; on adding water decolourised.	Little affected.	Fibre redder.	Little affected.				
Persian berries.	Not distinctive from quercitron and weld.		....	Fibre yellower.					

REACTIONS OF VEGETABLE COLOURS ON WOOL, MORDANTED WITH TIN SALTS.—*Continued.*

Colouring matter	Colours produced by various reagents.								
	Hydrochloric acid (sp. gr. 1.16)	Sulphuric acid (sp. gr. 1.84)	Nitric acid	Stannous chloride, hydrochloric acid, and water	Sodium hydroxide 10% solution	Boiling alcohol	Boiling soap (1% solution)	Boiling sodium carbonate (0.5 %) solution	Boiling 5% sulphuric acid solution
Turmeric...	Fibre reddish; solution pale pink; on dilution fibre bright yellow.	Fibre and solution reddish-brown; on dilution fibre pale straw; solution colourless.	At first deep red, then yellow.	Bright-reddish orange, fibre and solution.	....	Yellow solution; green fluorescence.	....	Orange solution; fibre light brown.	Pale-yellow solution; fibre paler; red orange on addition of sodium hydroxide.
Brazil wood.	....	Fibre brown; solution yellow to brown.	....	Fibre yellow.	....	Yellow.			
Campeachy wood.	Fibre crimson; liquid colourless.	Fibre and liquid dark maroon.	Brown.	Bluish-red.	....	No colour.	....	Fibre bluer; solution no colour.	
Orchil and cudbear.	Solution and fibre red.	Fibre and solution purple; solution on dilution red and fibre almost colourless.	Yellow.	Decolourised	Fibre and solution bluish-purple; color slowly removed.	Bluish-red solution.	....	Violet solution.	Orange solution; turned violet by sodium hydroxide.
Cochineal. .	Orange-red.	Dark violet.	Yellow.	Orange.	Red-violet.	No colour.			

on pages 383 to 434, the solutions containing them may be acidified with acetic acid and evaporated to dryness with a piece of wool mordanted with tin. The fibre is thoroughly washed and portions of it tested with reagents, the reactions of red colours being indicated on page 550 and yellow colours on page 578. Berry (*U. S. Dept. Agri., Bur. Chem., Circular* 25) observed the reactions indicated on pages 634–635 of the natural colours fixed upon mordanted wool.

Loomis (*U.S. Dept. Agri., Bur. Chem., Cir.* 63, pages 59 to 61) has published the reactions indicated on page 637.

The natural colours may also be fixed upon cotton mordanted with alum.

Formanèk (*Qualitative Spektralanalyse anorganischer und organischer Körper* 1905, pages 252 to 290) gives the absorption spectra of most of the natural colours.

Special Tests for Natural Colours.—*Archil* and *cudbear*, like the coal-tar colours, dye unmordanted wool red from an acid bath and may be stripped and re-dyed without much difficulty. The fibre becomes red when treated with dilute acid and purple with dilute ammonia. It is reduced by zinc and hydrochloric acid, and re-oxidised by exposure to air. Dilute nitrous acid turns the dyed fibre yellow. Ordinary archil is extracted from ammoniacal solution by amyl alcohol but sulphonated archil is not.

Tumeric is best extracted from food products (or their dried residues) by means of alcohol. The filtered extract is evaporated to dryness in a dish containing a few strips of filter-paper, these being then moistened with a dilute solution of boric acid acidified with hydrochloric acid, and again evaporated to dryness. In the presence of turmeric a cherry-red colour will develop which is changed to olive-green by alkalies.

Cochineal is readily identified by the orange colouration produced on treatment with acids and the violet with ammonia. The reaction with uranium acetate (see page 423) is very characteristic and reliable.

Alkanet is identified by its absorption spectrum and its reaction with ammonia (see page 432).

Chlorophyll is identified by its behaviour with solvents and most satisfactorily by its absorption spectrum. It is insoluble in water but soluble in alcohol, ether, ethyl acetate, acetone, amyl alcohol, petroleum ether glacial acetic acid and in solutions of the alkalies. It is usually found associated in plants with two yellow colouring matters,

APPEARANCE AND REACTIONS OF COLOURS IN AQUEOUS SOLUTION AND WITH CONCENTRATED SULPHURIC ACID.

Name of colour	Colour of aqueous solution	Add to aqueous solution			Zinc dust and HCl and expose to air on filter-paper	Dry colour + concentrated H_2SO_4	
		Hydrochloric acid (1.1) 5–10 drops	10% sodium hydroxide 5–10 drops	Ammonia (0.95) 5–10 drops		Before dilution	After dilution
Cochineal	Orange-red	Orange-yellow	Magenta	Magenta	Orange-yellow; not restored.	Pink	Yellowish-pink then straw-yellow.
Archil	Deep lilac	Yellowish-pink	Purple	Purple	Colour restored	Purple	Red. red-brown, orange.
Cudbear	Lilac	Yellowish-pink	Purple	Purple	Colour restored	Purple	Red-brown.
Logwood	Yellowish-brown.	Orange	Dark brown	Light brown	Colour not restored.	Yellow-brown	Paler.
Brazilwood	Red-orange, slight fluorescent.	Orange, not fluorescent.	Crimson	Crimson	Colour restored	Brown-yellow fluorescent.	Yellow not fluorescent.
Barwood	Insoluble	Colour ppt. on acidifying alkaline solution.	NaOH solution is deep brown-red.	Ammonia solution deep brown-red.	NaOH sol. + Zn dust decolourised; on exposure, pink then colourless.	Orange-brown.	Pink.
Poke berry	Crimson	Magenta	Orange-yellow	Magenta turning orange-brown.	Colour not restored.	Orange-brown.	Brown.
Spanish saffron	Yellow	No change	Paler	No change	Colour not restored.	Blue, purple, maroon, red-brown.	Yellow, then nearly colourless.
Quercitron	Brownish-yellow.	Slightly redder	Orange-brown	Orange-brown	Not decolourised	Yellow	Yellow
Sumac	Dirty yellow	No change	Greenish-brown	Yellow-brown	NaOH sol. + Zn dust decolourised; on exposure, pinkish then colourless.	Yellow	Yellow.
Annatto	Yellow in alkaline solution.	Paler			Zn + NaOH not decolourised.	Blue	Mauve.
Turmeric	Yellow in alkaline solution.	Paler			Zn + NaOH not decolourised.	Orange	Dirty yellow.
Persian berry	Yellow	No change	Orange	Deeper	Not decolourised	Yellow	Yellow.
Fustic extract	Yellow	No change	Brown-orange	Orange	Not decolourised	Yellow	Yellow.
Weld extract	Yellow	Paler	Deeper	Deeper	Not decolourised	Yellow	Yellow.
Buckthorn	Yellow	No change	Red-brown	Yellow-brown	Not decolourised	Yellow	Yellow.
Kamala	Yellow	Dilute alcohol solution of colour. Paler and cloudy.	Yellow-brown	Brownish-yellow.	NaOH solution of colour red, + Zn dust, orange. Original colour not restored.	Orange	Nearly colourless solution, orange ppt.
Catechu	Yellow-Brown	Paler, Cloudy	Dark Orange-Brown.	No Change		Brownish-Red.	Paler

carotin and xanthophyll which impart a yellowish tint to ordinary extracts of green plants. Solutions of chlorophyll usually have a strong red fluorescence, though this characteristic may, through the presence of a little copper or from some other circumstance, be lost and cannot be relied upon as a distinguishing mark. Chlorophyll readily decomposes, and after the death of the cell in which it exists a transformation to the brownish-green chlorophyllan commonly occurs, the brown colour of dried or cooked leaves being due to this substance. The presence of a little alkali prevents this change—a fact which is taken advantage of by cooks to preserve the green colour of cooked vegetables, a little soda being added to the water in which they are boiled. If fresh green leaves are extracted with alcohol made slightly alkaline with ammonia a fairly permanent pure green solution is obtained. If chlorophyll is treated with strong hydrochloric acid it splits up into two colouring matters the first of which (phylloxanthin) is brown and insoluble and the second (phyllocyanin) dissolving in the acid to form a blue solution, from which the colouring matter is precipitated on dilution.[1] The barium and lead compounds of chlorophyll are insoluble in alcohol.

The absorption spectrum of a newly prepared alcoholic extract of fresh green leaves in proper concentration exhibits 5 bands; a broad dark one at the Fraunhofer line C, 3 light ones (the first between C and D, the second close to D, and the third near E), and a fifth broad band beginning about F and taking in all the blue and violet. The appearance of this spectrum changes with the age of the solution, its concentration, and the nature of the solvent employed. The effect of age on chlorophyll solutions is to darken the spectrum band near E and to shorten the absorption in the blue sometimes splitting this into 2 bands. There is also slight alteration in the position of the other bands. Diluting the solution causes the disappearance of the light bands and a diminution of intensity of the dark ones, sufficient dilution effecting a separation of the absorption in the blue and violet into 2 bands. In the identification of chlorophyll it is advisable to

[1] Willstätter (*Ann.*, 1906 to 1908, **350**, **354**, **355**, **358**) has published some work which would indicate that chlorophyllan, phylloxanthin and phyllocyanin are mixtures. By decomposing chlorophyll with alkali he has obtained one series of compounds and with acid another series each of which have been successfully fractionated. He regards chlorophyll in plants as a mixture of an amorphous and a crystalline variety, the first being an ester of the unsaturated alcohol "phytol" and the second a magnesium compound. Literature-Tschirch, *Untersuchungen über das Chlorophyll*, 1884; Schunck and Marchlewski, *Chemistry of Chlorophyll*, *Roy. Soc. Pro.*, 1896, **59**, 233; Marchlewski, *Die Chemie der Chlorophylle und ihre Beziehung zur Chemie des Blutfarbstoffs*, 1909; Schryver, *The Chemistry of Chlorophyll*, *Sci. Prog.*, 1909, **3**, 425.

prepare for comparison a solution of that colour in the same solvent and of equal intensity to the unknown. Formanek (*Qualitative Spektralanalyse anorganischer und organischer Körper*, 1905) states that upon treating the solution with alcoholic potassium hydroxide and allowing the mixture to stand the absorption band in the red near C will be found to have divided into 2. He considers this quite characteristic, distinguishing chlorophyll from all other natural colours.

Caramel or burnt sugar is often used to colour food products, especially whiskey, brandy, cordials, vinegar, vanilla extract, and similar substances. In testing for caramel in liquids it is not permissible to concentrate the solution by evaporation on a steam bath as caramel may be formed from the carbohydrates present. If it is necessary to concentrate it should be done in a vacuum desiccator over sulphuric acid or at a temperature not exceeding 70°.

Amthor (*Z. anal. Chem.*, 1885, **24**, 30) tests for caramel as follows: 10 c.c. of the liquid are placed in a tall cylindrical vessel and treated with 30–50 c.c. of paraldehyde. Absolute alcohol is added in small portions, shaking vigorously after each addition, until the liquids mix. If caramel is present a brownish precipitate will settle out, depending in colour upon the amount of caramel present. The supernatant liquid is decanted and the precipitate washed twice with absolute alcohol, after which the residue is dissolved in a small amount of hot water and filtered. The colour of this solution will give some idea of the amount of caramel present. The colour may be identified by treating this filtrate with an equal volume of *freshly prepared* phenyl hydrazine reagent (2 parts phenylhydrazine hydrochloride, 3 parts sodium acetate, and 20 parts water) which in the presence of considerable caramel gives a dark brown precipitate in the cold, the reaction being hastened by warming. When small amounts are present the precipitate sometimes takes about 12 hours to collect.

Crampton and Simons (*J. Am. Chem. Soc.*, 1899, **21**, 355) treat 50 c.c. of the liquid with 25 grm. of Fuller's earth, shake vigorously, allow to stand for half an hour and filter. The colour of the filtrate should be compared in a tintometer with that of the original liquid and the percentage of colour removed by the treatment noted, this furnishing some indication of the proportion of colour due to caramel. All grades of Fuller's earth do not absorb caramel sufficiently to be employed in this test and the variety at hand should always be tested by control experiments before being used. The results obtained by

this test should be accepted with caution as the natural colour of some substances like vinegar (*J. Am. Chem. Soc.*, 1907, **29**, 75) are at times largely removed by Fuller's earth, and unless the liquid is almost decolourized (80% or more removed) it is not safe to conclude that caramel is present without confirmatory tests by another method.

Fradiss (*Z. Zuckerind.*, 1899, **28**, 229) tests for caramel in dry substances by extracting with warm, pure methyl alcohol. The brown solution is filtered, and chloroform or amyl alcohol added to the filtrate which causes a brown flocculent precipitate to form.

Woodman and Newhall (*Mass. Inst. Tech. Quarterly*, 1908, **21**, 280) found that in applying the Amthor test directly to vanilla extracts containing sugar the results are obscured by precipitation of the latter together with some of the natural colouring matter. This is true of many other preparations and their method of employing a preliminary treatment with zinc hydroxide is subject to fairly general application. They recommend that 15 c.c. of vanilla extract be mixed with 2 c.c. of zinc chloride (5% solution) and 2 c.c. of potassium hydroxide (2% solution). The precipitate is filtered, washed with hot water to remove sugar, and then dissolved in 15 c.c. of acetic acid (10% solution). This is concentrated to about half its volume, the excess of acid neutralised, and the solution divided between 2 test-tubes. To one of these 3 volumes of paraldehyde are added and just sufficient alcohol to make the mixture homogeneous. To the other is added an equal volume of *freshly prepared* phenylhydrazine reagent (see Amthor test immediately above). If caramel is present both tubes will exhibit a brown precipitate on standing over night.

Jagerschmid (*Z. Nahr.-Genussm.*, 1909, **17**, 269) proposes the use of a modification of Fiehe's artificial honey test in the detection of caramel.

Coal-tar Colours.

For a description of these, their constitution and properties consult pages 115, *et seq.*

Although the number of these dyes on the market is very great, and most of them, from a commercial standpoint, are suitable for colouring foods, it has been found that comparatively few are in common use. The following list includes most of those that have been sold on the American market for food purposes, the numbers being those

under which they are listed in Green's edition of Schultz and Julius, A Systematic Survey of Organic Colouring Matters, 1904, and the letters in brackets indicating the manufacturers as abbreviated in footnote.[1]

4 Naphthol yellow S (B).
8 Acid yellow (A).
9 Fast yellow (B).
10 Soudan G (A).
11 Soudan I (A).
13 Ponceau 4GB (A).
14 Orange G (A).
16 Butter yellow.
17 Chrysoidine Y (H).
18 Chrysoidine R (H).
49 Soudan II (A).
53 Palatine scarlet (B).
54 Scarlet GR (A).
55 Ponceau R, 2R, G, GR (A).
56 Ponceau 3R (A).
60 Scarlet 2R (CJ).
64 Crystal scarlet 6R (C).
65 Fast red B (B).
84 Resorcin yellow (A).
85 Orange I.
86 Betanaphthol orange.
89 Brilliant yellow S (B).
94 Tartrazine (B).
95 Metanil yellow (O).
97 Orange T (K).
101 Fast brown N (B).
103 Azorubin S (A).
104 Croceïn 3BX (By).
105 Fast red E (B).
106 New coccine (A).
107 Amaranth (M).
108 Scarlet 6R (M).
137 Resorcin brown (A).
139 Fast brown (By).
146 Brilliant croceïn M (C).
169 Croceïn scarlet 7B.
188 Naphthol black B (C).
197 Bismarck brown.
201 Bismarck brown R (H).
240 Congo red (A).
269 Chrysamin R (By).
287 Azo blue (By).
329 Chrysophenin (L).
398 Naphthol green B (C).
425 Auramine.
427 Malachite green (M).
428 Brilliant green (B).
433 Guinea green B (A).
434 Light green SF bluish (B).
435 Light green SF yellowish (B).
439 Cyanol extra (C).
440 New patent blue B, 4B (By).
448 Magenta (RH).
451 Methyl violet B (B).
452 Crystal violet (B).
462 Acid magenta (B).
464 Acid violet 4BN (B).
468 Acid violet 4B extra (By).
476 Methyl Alkali Blue (O).
480 Water blue (B).
502 Rhodamine G (B).
504 Rhodamine B (B).
510 Fluoresceïn.
512 Eosin (B).
516 Erythrosin G (B).
517 Erythrosin (B).
518 Phloxin P (B).
520 Rose bengal (B).
523 Rose bengal 3B (M).
584 Safranin.
601 Soluble indulines.
650 Methylene blue B, BG (B).
655 New methylene blue N (C).
667 Quinoline yellow (A).
692 Indigo carmine.

Pending further investigation, the United States authorities, in conformance to the provisions of the Food and Drugs Act of June, 1906, have prohibited the use of all coal-tar colours excepting the following 7, these being permitted provided they are certified to be true to name and to be free from mineral and metallic poisons, harmful organic constituents, and contaminations due to improper or incomplete manufacture: Amaranth (107), Ponceau 3R (56), Erythrosin

[1] The following abbreviations are employed for the names of the firms identified with the production of certain dyes: B. Badische Anilin und Sodafabrik. M. Meister, Lucius & Bruning (Höchst). A. Actiengesellschaft für Anilinfabrikation in Berlin. By. Farbenfabriken of Elberfeld Co., vorms. F. Baeyer & Co. C. Leopold Cassella & Co., Frankfurt. K. Kalle & Co., Biebrich. L. Farbwerke Mühlheim, vorms. Leonhardt & Co. C. J. Carl Jäger, Barmen. H. Read Holliday & Sons, Huddersfield. O. K. Oehler, Offenbach.

(517), Orange I (85), Naphthol Yellow S (4), Light Green SF Yellowish (435), and indigo disulphoacid (692), the numbers being the same as those referred to in the above table.

For *German laws* concerning food colours consult "*Vereinbarungen Untersuchung und Beurtheilung von Nahrungs- und Genussmitteln für das Deutsche Reich;*" for *French laws*, see Muttelet, *Ann. falsifications*, **2**, 26; for *Austria-Hungary* (*Bd. of Trade J.*, Aug. 23, 1906, Abs. *J. Soc. Chem. Ind.*, 1906, **25**, 857). In the United States many of the individual states have regulated the use of coal-tar dyes, and in Europe too there are local laws concerning them.

For the detection of coal-tar colours in foods 3 general methods are in use: First, dyeing wool by boiling the fibre in a solution prepared from the substance under examination; second, by extracting the colour by means of an immiscible solvent; third, by extracting the colour from the dried material by means of an appropriate solvent.

Method of Dyeing Wool.—This is the simplest and most easily applied test, and by stripping and redyeing on a second piece of wool serves to isolate the colour in a reasonably pure condition suitable for identification tests. Sostegni and Carpentieri (*Z. anal. Chem.*, 1895, **35**, 397) and Arata (*Z. anal. Chem.*, 1889, **28**, 639) have published the details of the method, the former employing a double dyeing and the latter only a single dyeing on wool.

Take about 50 c.c. of wine or other liquid, or about 30 grm. of jam, jelly, or ketchup, or about 20 grm. of syrup or confectionery, make up to 100 c.c. with water, acidify with 2–3 c.c. of 10% hydrochloric acid, add about 4 sq. in. of white wool (that has been freed from grease by boiling in water made faintly alkaline with potassium hydroxide), and boil for 10 minutes. Remove the wool from the bath, wash thoroughly in hot water, and strip the colour from the fibre by boiling in 100 c.c. of water containing 2 c.c. of strong ammonia (sp. gr. 0.9). Remove the wool, add enough dilute hydrochloric acid to render the bath slightly acid, add a fresh piece of cloth, and again boil for 10 minutes. In the presence of most coal tar colours except those of a basic character the second piece of wool will be dyed. A satisfactory second dyeing cannot be obtained with small amounts of sulphonated indigo.

With vegetable colouring matters except sulphonated archil this second dyeing gives practically no colour, though when large amounts of natural colour are present a dull stain is sometimes observed on the second piece of wool. When this occurs the thoroughly dried

fibre should be saturated with a few drops of concentrated sulphuric acid and allowed to stand for 5 minutes. At the end of this time the acid is pressed out with the blunt end of a glass rod and its colour noted. Vegetable stains char or discolour under this treatment while those coal tar colours which are not decolourised by strong sulphuric acid communicate a tint to the latter which remains on dilution with water. For the recognition of sulphonated archil see page 636. It should also be remembered that some coal tar colours are so altered by the acid or alkali employed in the double dyeing test that their presence is liable to be overlooked. Notable in this respect is Naphthol Green B which is destroyed by boiling with acids, and sulphonated indigo which is destroyed by prolonged boiling with alkalies. The former should be dyed from a neutral bath and the latter can be identified by its behaviour with reagents in the original solution and on the first piece of wool. The nitro colours are rendered fainter or decolourised by mineral acids, and dyes of the triphenylmethane series are similarly affected by alkalies.

The method of dyeing from acid solution will not serve to detect basic colours, and when negative results are obtained by it the process should be repeated, making the first dyeing from a bath rendered alkaline with 2 c.c. of strong ammonia, stripping with boiling 5% acetic acid, and redyeing from weak ammonia. It should be remembered that the basic colours are rendered fainter or decolourised by alkalies, the tint being restored by acetic acid.

Method of Extraction with Immiscible Solvents.—Loomis (*U. S. Dept. Agr., Bur. Chem., Circular* 35) has studied the behaviour of different colours with immiscible solvents and a review of his work indicates that amyl alcohol is the best of these for separating the dyes from aqueous solutions. Girard and Dupré (*Analyse des matieres alimentaires*, p. 169) also employ amyl alcohol and the experience of the writer would tend to recommend it.

If the solution of the substance under examination is rendered alkaline with sodium hydroxide and shaken with amyl alcohol in a separatory funnel, the fusel oil layer on separating will contain any basic colour that may be present together with some dyes of weakly acid character, though the presence of a basic dye in the amyl alcohol may not become evident until a little of it is shaken with dilute acetic acid to restore the colour. The amyl alcohol layer is separated and evaporated to dryness on a steam bath, this process being hastened by

the addition of a little ethyl alcohol from time to time. The residue is taken up in hot water and the colour fixed on wool from a bath weakly alkaline with ammonia in the case of basic dyes, and from a neutral or faintly acid bath in the case of weakly acid dyes. The basic colours may also be fixed from neutral solution upon cotton mordanted with tartar emetic and tannin.

If the alkaline solution from which the basic dyes have been removed is next rendered strongly acid (about 2 N) with hydrochloric acid and again shaken with amyl alcohol most of the acid colours will be taken up by the solvent, though some, like Acid Magenta and other highly sulphonated colours will scarcely be extracted at all. The presence of a little ethyl alcohol will cause a better extraction of the colour. The amyl alcohol layer is separated, shaken with dilute sodium hydroxide to remove the dye, the aqueous layer separated, acidified, and the colour fixed on a piece of clean white wool as directed on page 642. If the colour remains in the amyl alcohol after shaking with dilute sodium hydroxide, add an equal volume of petroleum ether and again extract; if the colour still remains in the amyl alcohol, the solvent must be evaporated on a steam bath and a dyeing made from the acidified[1] aqueous solution of the residue. Amyl alcohol takes up very few natural colours from alkaline solution, but on acidifying most of these are extracted (see page 633), and when they are present the double dyeing (page 642) should always be employed. As a general method for *detecting* acid colours in foods the use of immiscible solvents is not to be recommended.

Extraction of the Colour from the Dry Material.—This method is commonly employed in conjunction with that of dyeing wool, the colour being first extracted by some solvent and then fixed on wool. A general solvent for this purpose is 70% alcohol, the substance under examination being first reduced to as fine a state of division as possible and then macerated and shaken with about an equal volume of the alcohol until the colour is sufficiently extracted, this process being considerably expedited in the case of acid dyes by the addition of a few drops of ammonia. Mixtures of glycerol and water, or glycerol and alcohol are also employed as solvents, especially for meat products, and acetone is sometimes employed for cereal preparations.

To separate the colour from the alcoholic solution the latter is filtered and then evaporated to about one-third its original volume. The residue is made alkaline with sodium hydroxide and shaken with

[1] For dyeing fluoresceine derivatives the residue should be treated with weak ammonium hydroxide and then boiled with wool.

amyl alcohol to test for basic colours (page 643), the aqueous layer being then acidified and boiled with wool (page 642). If considerable dissolved organic matter is present, which often stains the wool on boiling over a free flame, it is advisable to heat on a steam-bath, replacing from time to time the water lost by evaporation.

Identification of Coal Tar Colours.—In identifying colours several facts must be borne in mind and carefully considered before arriving at a conclusion. The colour present may be a mixture like many of the browns which are compounded from blue, green, yellow, red, and orange, or, if a commercial dye were employed, the prevailing colour is apt to be modified in shade by admixture of a little of some other colour, this practice being known as "mixing to shade" (see page 440). Impurities such as resins, proteins, caramel, and natural stains should not be present on the fibre or in the solution with which identification tests are made or the results of these are apt to be misleading. In following the schemes mentioned below it is important to note the strength of reagents and the time allowed for the reactions by the authors, and since the colour changes described by them are influenced to a great degree by the amount of dye present, positive identifications should only be reported after comparing the reactions of the unknown colour to those of a known dye under like conditions and with like quantities of colour. Owing to the great multiplicity of names existing for the same colours, and the similarity of names for different colours (Orange R may be the sodium salt of either benzene azo-β-naphthol disulphonic acid R (H), sulpho-*o*-toluene azo-β-naphthol (I) or sulphoxylene azo-β-naphthol (B)), it is advisable to note the name of the firm manufacturing the particular one in mind.

Mixed colours can usually be detected by the different degrees of ease with which they are dyed on wool. By boiling several small pieces of wool separately in the same bath, allowing each piece to remain in it for about one minute, and preserving the order in which they were used, mixed dyes will be indicated by a gradual change in the colour of the fibre from the first to the last. By separating the pieces and selecting those containing the predominating amounts of the various shades, stripping, and redyeing in the same manner, a fairly satisfactory separation of the colours can often be obtained.

Basic colours may be separated from acid colours by rendering the aqueous solution alkaline with sodium hydroxide and shaking with two to three separate portions of ether. After separating and evapo-

rating the ether, the residue may be taken up in hot water and fixed upon wool or upon cotton mordanted with tartar emetic and tannin. The acid colours exhibit great diversity of behavior toward amyl alcohol, and a satisfactory separation can often be secured by taking advantage of this fact. The alkaline solution from which the basic colours have been extracted by ether is shaken with amyl alcohol which takes up a number of weakly acid dyes leaving those of more strongly acid character behind. The extraction with amyl alcohol from alkaline solution is repeated with fresh solvent until no more colour is removed. The aqueous solution is then neutralized and again extracted with fresh portions of amyl alcohol, the fusel oil extracts being kept separate from those obtained from the alkaline solution. The aqueous liquid is then acidified with acetic acid and extracted in a similar way, this being followed by 4 final extractions after the addition of increasing amounts of hydrochloric acid. The concentration of hydrochloric acid in the aqueous liquid should be at first about N/10, then N/2, then N, and finally about 2 N. A few of the highly sulphonated dyes will still remain in the aqueous layer after these successive extractions. The separations secured in this way are not always complete, but in general an indication of the proper further treatment is obtained. The dyes may be removed from their amyl alcohol solutions either by shaking with dilute sodium hydroxide (if necessary after the addition of an equal volume of petroleum ether) or, in the case of the strongly acid colours, by shaking with water, or by evaporating the solvent on a steam bath.

Some of the acid dyes like the non-sulphonated nitro-colours and the fluorescein derivatives form ether-soluble colour acids, and these may readily be separated from other acid dyes by shaking the acidified solution with ether. Upon shaking the ether solution of the colour acid with dilute ammonium hydroxide the dye will return to the aqueous layer and by evaporating this on a steam bath with a piece of wool the colour may be fixed on the fibre.

When the presence of a mixture has been established the best means of completely separating the constituent colours for identification can only be ascertained by experiment, and the procedure will vary with the particular mixture at hand. As an example of such separations, procedures for the seven colours permitted in the United States (see page 641) may be given, the methods being based upon their different chemical constitutions and upon a difference in their solubilities in common solvents, the procedure applying to the aqueous solutions of the colours.

Indigo disulphoacid and Light Green SF Yellowish may be separated from Naphthol Yellow S, Ponceau 3R, Amaranth, and Orange I by the action of a solution of sulphur dioxide and a little zinc dust, the blue and green being converted to colourless leuco compounds while the other dyes mentioned are destroyed. After filtering to remove excess of zinc dust, the blue or green may be restored in the filtrate by acidifying with a little acetic acid and boiling.

Erythrosin may easily be separated from all the other permitted colours owing to the fact that its colour acid is readily soluble in ether. On acidifying slightly with acetic acid and shaking with ether in a separatory funnel, the erythrosin colour acid passes into the ether layer, which may be separated and washed with water containing a little acetic acid. On shaking with weak ammonia the erythrosin passes into the aqueous layer.

Orange I may be separated from all the other permitted colours except erythrosin by acidifying slightly with acetic acid and shaking with amyl alcohol. The colour acid of Orange I passes into the amyl alcohol, which may then be washed with water containing a little acetic acid, and on being shaken with weak ammonia water the colour returns to the aqueous layer, a distinction from Orange II, which must be shaken with dilute sodium hydroxide in order to make the colour return to the aqueous layer.

Ponceau 3R forms a very insoluble barium salt by means of which it may be separated from all the permitted dyes except indigo disulphoacid. On adding a solution of barium acetate or chloride to the colour solution a flocculent lake containing the Ponceau forms and may be filtered off. A considerable excess of the barium reagent favours flocculation of the precipitate, which in very dilute solutions containing other colours sometimes requires 1–2 hours to form. The lake is washed with cold water, dissolved in dilute hydrochloric acid, and the colour fixed on wool by boiling in this solution.

Naphthol Yellow S may be separated from the azo dyes (Orange I, Ponceau 3R, and Amaranth) by adding ammonia to the solution, boiling, and adding bromine water, a few drops at a time, until, after about 30 seconds' boiling, only a pure yellow colour remains. The boiling is continued for 3–4 minutes to remove excess of bromine, and the solution may then be acidified and the Naphthol Yellow S fixed on wool.

Naphthol Yellow S may be separated from Light Green SF Yellowish

by acidifying 50 c.c. of the solution with 5 c.c. of 1–5 sulphuric acid and shaking with amyl alcohol. The amyl alcohol is washed once or twice (according to the amount of green present) with 50 c.c. of water containing 2 c.c. of 1–5 sulphuric acid, and then with 50 c.c. of pure water. The yellow passes into the amyl alcohol from the dilute acid, but returns to the aqueous layer on shaking with pure water.

Amaranth may be separated from Naphthol Yellow S by acidifying 50 c.c. of the solution with 5 c.c. of 1–5 sulphuric acid and shaking with two 25 c.c. portions of amyl alcohol. The yellow is removed by the amyl alcohol.

Indigo disulphoacid may be destroyed in any mixture of dyes by treating the boiling solution with a little acetic acid and a few drops of 1% sodium nitrite solution. If the amount of indigo is very small it may also be conveniently destroyed by boiling with very dilute solutions of the alkalies.

Further means of separating mixed dyes have been given by Rota and appear on page 474.

Schemes for the Identification of Colours.—Several of these have already been given, that of Weingärtner on page 444, Witt's on page 447, Green's page 459, and Rota's on page 463, and they may be employed on solutions of the colour separated from the foodstuff by any of the means given above, observing the precautions mentioned on page 645, and remembering that these schemes were elaborated with solutions containing much more colour than is commonly obtained from foods. Many schemes have been published for the identification of dyes on the fibre, references to these having been given on page 485. An excellent and systematic method has recently been published by A. G. Green (see pages 435 to 438). On pages 540 to 621 may be found the behaviour of dyes on fibre when treated with various reagents. Circular 63, *U. S. Dept. Agri., Bur. Chem.*, by H. M. Loomis, and "The Indentification of Pure Organic Compounds, Vol. III, 1910, by S. P. Mulliken, are entirely devoted to the identification of coal-tar colours.

The spectroscope may also be employed for identifying colours, a description of this method appearing on pages 435 to 438. More recently Formanèk (*Spektralanalytischer Nachweis künstlicher organischer Farbstoffe*, 1900) has published an elaborate work for the spectroscopic recognition of colours. By means of this instrument and according to the form of the absorption bands, he divides all colours into groups and

sub-groups, the greens into six chief groups, blues into eight, reds into six, and yellows into five. Having ascertained the group, the positions of the absorption bands in the spectrum are next determined, and this with the help of the author's tables is often sufficient to identify the individual colour. In case of doubt the solution is divided into three parts, dilute nitric acid (1–5) being added to one portion, ammonia water (sp. gr. 0.96, 1–5) to the second, and potassium hydroxide (1–10) to the third. The colour changes in the solution and also the alteration in the positions of the absorption bands are observed. All these have been noted by the author and by the use of his tables he is able to identify all colours except a few of the yellow and brown series which are insufficiently characterized by these tests. Of prime importance in this work are the nature of the solvent and the strength of the solution or the section through which this is observed. The character and position of the absorption bands for the same colour are often different in different solvents, and the author has recorded these for water, ethyl alcohol, and amyl alcohol. The strength of the solution also modifies the bands considerably. If it is too weak some of the lighter bands are apt to disappear, if too strong the bands often become ill-defined and the so-called double bands appear as one. In practice it is well to start with a fairly strong solution and gradually dilute until the proper definition is obtained. The same effect is secured by the use of a triangular cell, which by a forward or backward movement brings sections of various depths in front of the slit.

Flesh Foods.—Sausages, canned goods, and fish pastes are sometimes coloured, the colours used being red ochre, or some other red pigment, cochineal or cochineal lake, carmine, and coal tar dyes such as Fuchsin, Diamond Red, Safranin, eosines, ponceaus, Bordeaux reds, Benzopurpurin, and various mixtures. Sausage casings are sometimes coloured to simulate a smoked appearance. Meat occasionally presents an abnormal appearance not due to added colour on account of the animal having suffered from acute fever, diseases of various kinds, or because of being overdriven or of insufficient bleeding after slaughter. Lipochrome is a red colouring matter existing in the tissues of fishes, while healthy oysters may exhibit a green colour due to the pigment marennin.

Red ochre may be detected by the abnormal amount of iron in the ash. It may also be found by examination of the ground sample under a microscope, the particles of pigment becoming visible at a magnifica-

tion of 120–160. By mounting in concentrated hydrochloric acid and heating over a small flame and subsequently introducing a little potassium ferrocyanide reagent at the edge of the cover-glass, Prussian blue is seen to form as the reagent diffuses inward.

Cochineal lake is detected by macerating the preparation, previously freed from fat by treatment with ether, in water containing about 2% absolute HCl, and shaking the strained liquid in a separatory funnel with amyl alcohol. The amyl alcohol layer is washed with successive portions of water to remove the mineral acid and tested for cochineal with ammonia and with uranium acetate (page 423). The metallic base of the lake may be detected in the ash.

Marpmann (*Z. angew. Mikrosk.*, 1895, page 12) examines a thin section moistened with 50% alcohol under the microscope, which usually reveals artificial colour, as the natural colour of meat is bleached by this treatment. If only traces of dye are present some of the material is clarified by xylol and the latter removed by CCl_4. On mounting in cedar oil the mass, now transparent, reveals the presence of foreign colour, fuchsin, carmine, logwood, and archil staining the cell substance while acid dyes colour the liquid cell contents.

Cochineal carmine may be detected by heating 20 grm. of the finely ground material with equal parts of glycerin and water on a steam bath. Filter and extract the cochineal from the glycerin-water mixture, with amyl alcohol, further treatment being the same as just given under cochineal lake. In many cases 50% alcohol may be substituted with advantage for the glycerin-water mixture.

Coal-tar colours may be extracted from the finely chopped meat or sausage casing by digesting with 50% alcohol. On evaporating off the alcohol some fat may separate out and this should be removed by filtering. The filtrate should be tested by boiling with wool fibre as described under general methods, page 642.

See also: Colour in sausages, O. Klein, *Z. Nahr. Genussm.*, 1909, **18**, 364; detection of coal tar dyes in sausages, A. Kickton and W. Koenig, *Z. Nahr., Genussm.*, 1909, **17**, 433; detection of artificial colour in sausage casings, T. Merl, *Pharm. Centrh.*, **50**, 215.

Canned Vegetables.—Copper is commonly used to impart a bright green colour to pease, beans, spinach, and Brussels sprouts, and in such cases is found in the solid matter alone, the liquor rarely containing any of the metal. For its detection and estimation, 100 grm. of the drained vegetable are placed in a porcelain dish and reduced to an

ash at a low red heat. The ash is moistened with strong hydrochloric acid, about 25 c.c. of water added, and the whole digested on a steam-bath. The solution is filtered and the residue on the filter washed, after which the latter is replaced in the dish and ashed a second time to consume any unburned carbon. The ash is treated with hydrochloric acid as before, and the filtrate from this solution added to the first. Hydrogen sulphide is passed through the combined filtrates which have previously been warmed, the copper sulphide that separates is collected on a filter, washed, and finally ignited in a small porcelain crucible. The residue is dissolved in a small amount of nitric acid and the copper determined iodimetrically (see Sutton, *Volumetric Analysis*, 1907, p. 188), by titration with KCN (*Ibid.*, page 190), or colourimetrically (*Ibid.*, page 197). The copper may also be estimated in nitric acid extracts of the ash by well known electrolytic methods.

Occasionally coal tar colours are met with in tomatoes, tomato pastes, radishes, and peppers. Vegetables of firm consistency like radishes are passed through a sausage grinder and then extracted with 80% alcohol. The extract is filtered and the colour fixed on wool by the procedure given under general methods page 644. Soft vegetables like tomatoes may be reduced to a pulp, enough water added to make them fairly fluid, and wool dyed by boiling directly in this mixture according to the General Methods on page 642.

Noodles, Macaroni, Pastry, Biscuits, Cereal Products, Cattle Feed, etc.—Saffron, turmeric, annatto, Naphthol Yellow S, Victoria Yellow, Martius Yellow, Metanil Yellow, Orange I, Orange II, Quinoline Yellow, the tropaeolines, picric acid, and Tartrazine have been used in these products. The detection of artificial colours is complicated by the presence of the natural colouring matter of flour and sometimes that of eggs. As both of these are soluble in ether a previous extraction with that solvent serves to remove a large amount of the interfering substances without appreciably affecting the artificial colours.

The coal tar colours are readily extracted from the finely ground material by maceration for about 12 hours with 70% alcohol as directed on page 644.

Reichelman and Leuscher (*Z. Nahr.-Genussm.*, 1903, 6, 175) heat 50 grm. of the ground material with 75 c.c. of acetone for one hour under a reflux condenser. The acetone is then decanted into another flask and distilled. Thirty c.c. of hot water are added to the residue and after cooling the mixture is freed from fat by filtering. The

filtrate, containing the artificial colouring matter, is tested by boiling with wool (page 642) for coal tar colours, and for vegetable colours as indicated on pages 632, *et. seq.*

Fresenius (*Z. Nahr.-Genussm.*, 1907, **13**, 132) extracts 20–40 grm. of the powdered material with ether in a continuous extraction apparatus. The ether is removed from the residue by drying in a water oven, and it is then shaken for 15 minutes with 120 c.c. of 60% acetone and allowed to stand for 12 to 24 hours. At the end of that time the mixture is filtered and the filtrate heated on a steam-bath to remove acetone. The aqueous residue is divided into two portions, one larger than the other. To the larger portion sufficient acetic acid is added to dissolve any solid matter that has separated, and it is then boiled with clean white wool. If the wool is dyed by this treatment the colour should be purified by a second dyeing as described on page 642. If a negative test is obtained and artificial colour is suspected the bath should be made alkaline with ammonia and tested for basic colours as indicated on page 643.

To the smaller portion of the aqueous residue left after removal of the acetone, an equal volume of alcohol is added and the mixture warmed to dissolve flocks. It is then divided into four parts, one of which is reserved for comparison, hydrochloric acid is added to the second, ammonia to the third, and stannous chloride to the fourth. The natural colour of flour is decolourised by hydrochloric acid, intensified by ammonia, but is not affected by stannous chloride. Saffron acts similarly but is not decolourised by hydrochloric acid.

Juckenack (*Z. Nahr.-Genussm.*, 1900, **3**, 1) shakes one 10 grm. portion of the finely ground material with 15 c.c. of ether, and another portion with 15 c.c. of 70% alcohol and allows both to stand for 12 hours. If the ether remains uncoloured or almost so, while the material is distinctly tinted, and the alcohol is coloured while the material is almost decolourised, a foreign colour is indicated. If both the ether and alcohol are coloured, egg colour with or without foreign colour is present. A portion of the ether solution treated with dilute nitrous acid is decolourised in the presence of egg colour alone. If artificial colour is indicated the portion treated with ether is extracted with three or more fresh portions of the solvent and then shaken with 70% alcohol and allowed to stand for 12 hours. It is then filtered, the filtrate acidified slightly, and boiled with clean white wool. The colour is purified as directed on page 642. To detect basic colours the alcohol

extract should be rendered alkaline with ammonia and again boiled with wool (see page 643).

Piutti and Bentivoglio (*Gaz. chim. Ital.*, 1906, **36**, (II), 385) give a method for detecting Martius Yellow, Victoria Yellow, picric acid, and Metanil Yellow which are prohibited by Italian law, and for distinguishing these from Naphthol Yellow S which is permitted. Fifty grm. of the material are boiled with 500 c.c. of water and 2 c.c. of strong ammonia water, and after adding 60–70 c.c. of alcohol the boiling is continued for 40 minutes. The mixture is filtered and the filtrate acidified with 2–3 c.c. of dilute hydrochloric acid after which it is boiled with 25–30 grm. of clean white wool. The colour is stripped with ammonia and redyed on fresh wool (see page 642), and again stripped with ammonia. This last solution is evaporated to dryness and the residue taken up in water and filtered. If insoluble matter has formed, treat some of it with dilute hydrochloric acid, which in the presence of Metanil Yellow gives a violet colouration, and another portion with ammonium sulphide which with picric acid turns brown. To a little of the filtrate stannous chloride is added, and when the mixture has become colourless this is followed by sodium hydroxide. The nitro colours produce a red colouration. Another portion of the filtrate is acidified with hydrochloric acid which in the presence of Metanil Yellow produces a violet colour. If any of these colours are indicated the remainder of the filtrate is acidified with acetic acid and shaken with carbon tetrachloride which extracts Martius Yellow and Victoria Yellow, and does not extract picric acid, Metanil Yellow or Naphthol Yellow S. If the colour is extracted, the carbon tetra chloride is separated and shaken with dilute ammonia. The ammonia is concentrated and divided into two parts, to one of which, after acidifying with hydrochloric acid, stannous chloride, and then ammonia water are added. A rose colouration indicates Martius Yellow. To the other hydrochloric acid and zinc dust are added which in the presence of Victoria Yellow causes a rose-violet colouration.

If the colour is not extracted by carbon tetra chloride the aqueous layer is evaporated to dryness, again taken up in water, and the solution divided into three parts. One is treated with hydrochloric acid, with which Metanil Yellow produces a violet colour, the second is treated with ammonium sulphide, with which picric acid becomes red-brown, and the third is heated with zinc dust and ammonia,

filtered, treated with zinc dust and hydrochloric acid, again filtered, and the filtrate divided into two parts, one of which in the presence of Naphthol Yellow S becomes yellow on treatment with potassium hydroxide, and the other orange with ferric chloride.

Turmeric may be detected by extracting the ground material with 90% alcohol and testing the alcoholic solution with boric acid (see page 636).

Saffron may be extracted from the ground material by allowing it to stand with 90% alcohol for 12 hours. On filtering and evaporating off the solvent from the filtrate the dry residue is treated with a drop of sulphuric acid. In the presence of saffron an *immediate* pure blue colour appears which is very fugitive. A drop of concentrated nitric acid also produces an immediate blue colour which is even more fugitive than that given by concentrated sulphuric acid. These colours are produced instantaneously and should not be confused with those which develop on standing and which are caused by other extractive matter. If much of the latter is present it tends to obscure the test and the dry residue should then be washed with ether to remove fat, after which it is dissolved in a little dilute alcohol, acidified, and shaken with amyl alcohol. The amyl alcohol layer is separated, washed once with water and then evaporated to dryness on a steam bath, adding a little alcohol from time to time to hasten the evaporation. This residue may be tested with sulphuric and with nitric acid as mentioned above.

Wines.—These have been considered in Vol. I, pages 177–182.

The Paris Municipal Laboratory employs three preliminary tests for the detection of artificial colour in wines.

(1) Sticks of chalk are steeped in a 10% solution of egg albumin and dried, first in the air and then at 100°. A piece of this chalk is scraped to remove excess of albumin adhering to its surface and two drops of the wine applied. Genuine wines produce a gray or sometimes a bluish tint, but there should be no sign of green, violet, or rose colour.

(2) The wine is made alkaline with a solution of barium hydroxide and shaken with amyl alcohol. The amyl alcohol is separated and then shaken with acetic acid. Basic dyes are indicated by the appearance of colour in the amyl alcohol either before or after treatment with acetic acid.

(3) Potassium hydroxide (5%) is added to 10 c.c. of wine until the

colour becomes green, and then 2 c.c. of mercurous acetate solution (20%) are added. The mixture is shaken and filtered. Pure wines give a colourless filtrate both before and after acidifying with hydrochloric acid, while the acid coal tar colours tint the filtrate red or yellow.

Basic dyes may be fixed on wool from the residue left after evaporation of the amyl alcohol from the alkaline extraction of the wine. Acid dyes should be fixed on wool by the double dyeing method indicated on page 642.

Vegetable colours may be detected by acidifying the wine with hydrochloric acid and extracting with amyl alcohol. This should be further treated as indicated on pages 632-639, the colours to be particularly sought being cochineal, alkanet, and archil (both natural and sulphonated).

Blyth (*Foods, their Composition and Analysis*, 1903, page 461) gives an elaborate scheme by Gautier for the detection of artificial colour in wines which includes many of the less known vegetable colours. See also: Detection of Bilberry Juice in Red Wine, Plahl, *Z. Nahr.-Genussm.*, **15**, 262; and Chicory Colour in White Wines, Popescu, *Ann. chim. anal.*, **13**, 101.

Brandy, Rum, Whiskey, Liqueurs, Cordials, Vinegar, Fruit Syrups, Flavoring Extracts.—Caramel is commonly used to colour brandy and whiskey and to some extent also the other products under this heading, particularly factitious vinegar and vanilla extract. The liqueurs may contain either coal tar or natural colours; artificial fruit flavours are commonly tinted with coal tar dyes. The brown dyes occasionally found in brandy, rum, and whiskey, and the green colours of cordials are apt to be mixtures and the methods of detection outlined on pages 645 to 648 should be followed.

Basic coal tar colours may be detected by making the liquid under examination alkaline with ammonia and shaking with amyl alcohol, diluting the mixture with water if necessary to prevent a mingling of the two layers. The amyl alcohol is separated and shaken with 5% acetic acid. A bright colouration of the amyl alcohol either before or after treatment with acetic acid indicates a basic colour. This should be confirmed by fixing on fibre as indicated on page 643.

Acid colours are detected by diluting about 20–50 c.c. of the liquid with water to reduce the concentration of alcohol or sugar, acidifying, and subjecting to the double dyeing method (page 642).

Vegetable colours may be tested for directly in such preparations as

contain very small amounts of dissolved solids, it being advisable in most cases to concentrate by evaporation before applying any tests. When sugar and other extractive matter is present the separation with amyl alcohol from acid solution (page 632) is employed. Saffron may be shaken out of the neutral solution with amyl alcohol, and the residue left after evaporation of the latter tested with concentrated sulphuric and with concentrated nitric acid (see page 654). This last serves as a means of detecting the nature of a common green mixture composed of saffron and indigo carmine, the saffron being taken up by the amyl alcohol in neutral solution while the indigo carmine can be fixed on wool by boiling the fibre in the solution left after removal of the saffron.

Chlorophyll is detected as indicated on page 636.

Tests for caramel have been described on pages 639–640. In applying the Amthor test it should be remembered that the paraldehyde mixture has a tendency to precipitate sugar and gums, and these may carry with them some natural colour which often gives false indication of caramel. Schidrowitz (*J. Soc. Chem. Ind.*, 1902, **21**, 816) has stated that Amthor's test may show caramel when there is none and fail to discover it when actually present (see Vol. 1, page 179). In such cases the procedure of Woodman and Newhall (page 640) is to be recommended. Vanilla extract containing only natural colour, when deprived of its alcohol by evaporation and restored to its original volume with water, on treatment with an excess of basic lead acetate and filtering should yield a colourless or pale straw-coloured filtrate. In the presence of caramel this filtrate is brown, varying in shade according to the amount of caramel present.

For the detection of caramel in spirits the paraldehyde test as modified by Lasche (*Brewer Distiller*, May, 1903) and the modified Marsh test (*Pro. A. O. A. C.*, 1908) may be mentioned. To 5 c.c. of the whiskey contained in a test-tube 10 c.c. of paraldehyde are added, followed by absolute alcohol, 2–3 drops at a time, shaking vigorously after each addition of the latter until the mixture becomes clear. The whole is now set aside for ten minutes when, if a turbidity has appeared, caramel is indicated.

The Marsh test depends upon the solubility in amyl alcohol of the colour extracted by spirits from the wooden containers in which they are stored. The reagent is prepared by adding 3 c.c. of syrupy

phosphoric acid and 3 c.c. of water to 100 c.c. of pure redistilled amyl alcohol. The reagent should be shaken immediately before using. 50 c.c. of the whiskey are evaporated just to dryness on a steam-bath, and the residue dissolved in 26.3 c.c. of 95% alcohol. The solution is transferred to a 50 c.c. flask and made up to volume with water. 25 c.c. of this solution are placed in a separatory funnel and lightly shaken with 20 c.c. of the Marsh reagent so as not to form an emulsion. The layers are allowed to separate and the operation of shaking and standing repeated twice again. After the layers have completely separated for the last time the aqueous solution containing the caramel is drawn off into a 25 c.c. cylinder and made up to mark with 50% by volume alcohol. The colour of this solution is compared in a colorimeter with that of the 25 c.c. not treated with the Marsh reagent, and the proportion of colour insoluble in amyl alcohol calculated. With whiskey stored in plain or charred oak barrels this amounts to less than 10% but when old sherry casks have been used, it sometimes reaches 25%.

Confectionery.—Owing to the wide range of materials that enter into the composition of confectionery considerable discretion must be employed in its examination for artificial colours and no unvarying method can be prescribed. All kinds of colouring matters have been used and the water-insoluble material should be examined for pigments and lakes in addition to the customary search for the soluble colours. Portions of different colour and composition may often be separated from each other mechanically, avoiding the subsequent chemical separation of mixed colours, and separating water-soluble portions, which may be treated directly, from the solid portions which require a previous extraction of the colouring matter by means of a solvent. Frequently the colour is found confined to a thin outer layer which is readily washed off.

In general the separated material should first be digested with warm water and filtered. The filtrate is examined by the double dyeing method (page 642), and by extraction with amyl alcohol (page 643). The residue is digested with strong alcohol and again filtered. The filtrate is heated on a steam-bath to drive off most of the alcohol, diluted with a little water and then examined by the same methods as the previous filtrate. The residue, if still coloured, may contain coloured lakes and should be treated with tartaric, oxalic, or hydrochloric acid to release the colour from its metallic base, after which the

dye may be extracted with amyl alcohol as indicated on pages 643 and 644. Pigments are detected by examining the water-insoluble portion of the material (separated by decantation, filtration, or the use of the centrifugal machine) under the microscope, or by an analysis of the ash, the former generally indicating only the presence, but the latter also the nature of the pigment.

Cane sugar frequently contains a little blue pigment, usually ultramarine, which may be detected by dissolving a large sample in water and allowing it to settle for 10 to 12 hours, when the pigment will be found on the bottom of the container.

Candied Fruits and Flowers.—These are quite commonly coloured, such products as maraschino cherries, candied violets, and roses almost invariably so. They should be finely divided, digested with strong alcohol until the colour has been sufficiently extracted, and filtered. The filtrate is heated on the steam-bath to remove most of the alcohol, diluted with a little water, made alkaline with ammonia, and extracted with amyl alcohol to detect basic colours (page 643). The aqueous layer is then subjected to the double dyeing test (page 642).

Tea.—If 20–30 grm. of the tea be stirred for a few minutes with about 100 c.c. of hot water and then strained through a 40-mesh sieve, the tea being washed upon the sieve with about 200 c.c. of hot water, the pigments composing the facing will pass through into the strained liquor and may be collected by allowing them to settle or, better, by whirling in a centrifugal machine. Upon examining the sediment under the microscope particles of Prussian blue are seen to lose their colour when treated with sodium hydroxide. Indigo is not affected. Prussian blue also differs in its appearance, under the microscope, being transparent and blue, while indigo has a greenish hue and is almost opaque. Talc is seen as irregular, colourless, translucent particles.

Coffee.—In a manner analagous to the facing of tea various pigments have been applied to the surface of coffee beans (compare Vol. VI. These may be detected by an examination of the ash or by a microscopical examination of the sediment obtained by soaking the beans in water, straining through a sieve, and centrifuging or filtering the strained liquor. Organic colouring matters are extracted by treatment with alcohol as described on page 644.

Coffee essence often contains caramel added to impart a deceptive

appearance of strength. This is detected by diluting the essence with an equal volume of water, adding an excess of basic lead acetate, and shaking. On allowing the precipitate to settle the clear liquid will be almost or quite colourless if coffee alone has been used, but will be brown or deep yellow in the presence of caramel.

Cocoa and Spices.—Ground spices sometimes contain pigments and lakes, brick dust, charcoal, red sandalwood and other brown and red woods, turmeric, and coal tar dyes. The microscope or an examination of the ash usually serves for the detection of all except the dyes, though the stained tissues sometimes indicate the presence of these also. The coal tar dyes are best extracted by means of alcohol as described on page 644, the filtered alcoholic solution being subjected to the double dyeing process described on page 642. Alcohol alone often suffices to extract colours from lakes but sometimes treatment with tartaric or hydrochloric acid is required to attack the metallic base (see under Confectionery, page 657).

Winton (*Microscopy of Vegetable Foods*, 1906, page 522) boils wool directly in a thin paste prepared by mixing the powdered spice with a 1% solution of potassium acid sulphate.

Turmeric may be detected in the alcoholic extract by means of the boric acid test (page 636).

La Wall (*Am. J. Pharm.*, 1907, **79**, 326) mixes 15 c.c. of alcohol with 2 c.c. of carbon disulphide and adds 2 grm. of the suspected spice. The mixture is shaken thoroughly, and then 5 c.c. of melted lard or liquid petrolatum are added and the whole again shaken vigorously for several minutes. After allowing the mixture to stand, the alcohol layer is separated and tested in the usual way for artificial colour.

Milk.—Leach (*J. Am. Chem. Soc.*, 1900, **22**, 207) takes about 150 c.c. of milk, adds a small amount of acetic acid and heats in a porcelain casserole over a Bunsen flame. By means of a stirring rod the curd that forms can nearly always be gathered into one mass, after which the whey is simply poured off. If the curd remains in flocks it is strained through a sieve or collander. All of the annatto or the coal tar dye in the milk so treated will be found in the curd and part of the caramel. The curd, pressed free from adhering liquid, is picked apart, if necessary, and shaken with ether in a corked flask in which it is allowed to soak for several hours, or until the fat has been extracted and with it the annatto. If the milk is uncoloured, or has been coloured with annatto, on pouring off the ether the curd should be left perfectly

white. If, however, a coal-tar dye or caramel has been used, after pouring off the ether the curd will be coloured more or less deeply. Thus ether extracts annatto along with the fat from the curd, but does not extract the coal-tar dyes or caramel. The ether extract containing the fat and annatto, if present, is evaporated on a water-bath, the residue is made alkaline with sodium hydroxide and poured upon a small wet filter, which holds back the fat but allows the aqueous portion to pass through. On washing off the fat gently under a water tap, all of the annatto of the milk used for the test will be found to have been concentrated upon the filter, giving it an orange colour. Upon applying a drop of stannous chloride solution to the paper a characteristic pink colour is produced.

If the milk has been coloured with an azo dye the coloured curd, on applying strong hydrochloric acid in a test-tube will immediately turn pink. If caramel is present the acid solution of the coloured curd will gradually turn blue. This blue colour forms more readily the more thoroughly the fat has been extracted, and is not indicative of caramel except when the curd is coloured. Caramel should be confirmed by taking 100 c.c. of the original milk and curdling by adding 100 c.c. of alcohol. The whey is filtered off, and a small quantity of basic lead acetate added to it. The precipitate thus produced is collected upon a small filter, which is then dried in a place free from hydrogen sulphide. A pure milk thus treated yields upon the filter-paper a residue which is either wholly white, or at most a pale straw colour, while in the presence of caramel the residue is more or less of a dark brown colour according to the amount of caramel used.

Blyth (*Foods, Their Composition and Analysis*, 1903) detects colouring matters in milk as follows: Sulphonated azo dyes impart a pink colour when the milk is treated with hydrochloric acid. Confirm by extracting as below and apply the usual tests.

A piece of filter-paper soaked for 24 hours in the milk made alkaline with sodium carbonate takes a brown stain which is changed to pink by hydrochloric acid—presence of annatto. Confirm by extracting as below and applying the following tests:

(a) A drop of the colouring matter dissolved in water and made alkaline with potassium hydroxide gives an orange stain on filter-paper which is changed to pink by stannous chloride. (b) A little of the residue is dissolved in water containing a little alcohol and a drop of ammonia. A bundle of white cotton fibres is introduced and the

liquid evaporated nearly to dryness. The fibre is then immersed in a solution of citric acid. It will be coloured rose-red if annatto is present.

Caramel.—Coagulate 10 c.c. of the milk by means of acetic acid, collect the curd by straining through linen, then place in a white porcelain casserole and just cover with strong hydrochloric acid. Treat a control sample known to be free from caramel in the same manner—a blue-violet colour indicates caramel.

Other colouring matters may be present or the original presence of certain coal-tar dyes may be masked by the sample being partly decomposed, since it has been shown (Blyth, *Analyst*, 1902, **27**, 146) that certain coal-tar colours are reduced very rapidly in decomposing milk under the influence of nascent hydrogen set free by the action of anaerobic organisms. For the isolation of colouring matters and their decomposition products the following method may be used: Take at least 60 c.c. of milk, carefully add to it weak sodium or potassium carbonate solution until it is just alkaline to delicate litmus paper. Evaporate the solution to a thin paste on a water-bath.

(a) Thoroughly extract the paste with ether. This will remove the fat and, if the milk was sour, the decomposition products of those dyes reduced by nascent hydrogen. Evaporate off the ether and shake the fat in a separatory funnel with warm water. Separate the water from the fat and evaporate the water to dryness in a porcelain dish; note the colour of the residue, pure milk yielding no coloured residue, and consult the following table:

(b) Extract the fat-free residue with boiling alcohol, filter and evaporate to dryness in a white porcelain dish. A portion of the residue, if yellow or orange, may be taken up with a little N/10 acid and shaken with ether; this will divide the possible dyes into 2 groups, *i. e.*: (1) The natural colouring matters (annatto, turmeric, saffron, etc.), the azo dyes and the nitro dyes which all colour the ether to a certain extent. (2) The basic dyes and the sulphonated azo dyes which do not colour the ether at all. The sulphonated azo dyes will be readily recognised by striking brilliant colours with the acids, and the other dyes may be recognised by the ordinary methods.

A. WATER EXTRACT FROM THE FAT.

Note the colour and apply various reagents to the dry residue.

Colour of residue	Probable original colouring matter	Add drop of ferric chloride	To the ferric chloride add strong sulphuric acid	Other reactions
Brown........	Acid Yellow...	Dark green. .	Yellow, green on dilution.	
Brown.........	Butter Yellow.	Dark blue-green.	Yellow, green on dilution.	To slightly acid solution of the colouring matter add a few drops of hydrogen sulphide solution, then ferric chloride, heat—magenta color.
Brown........	Aniline Yellow.	Yellow.......	Yellow.......	Strong sulphuric or hydrochloric acid gives delicate violet.
Yellow	Martius Yellow	Red..........	Yellow.......	Stronge hydrochloric acid gives a beautiful rose-red color.
Yellow........	Victoria Yellow.	Red.........	Yellow.......	Same as Martius Yellow.
Rose red......	Methyl Orange	Fugitive scarlet.	Yellow.......	Treat as with butter yellow; the solution becomes a beautiful blue.
Brown-red	Orange IV....	Green........	Scarlet, green on dilution.	Treat as butter yellow; the solution becomes a dirty violet.
Yellow........	Unreduced dyes, soluble in ether from alkaline solution.			

B. ALCOHOL EXTRACT, COLOURED ORANGE, YELLOW, OR BROWN.

Take up a portion of the residue with dilute sulphuric acid and shake with ether.

(1) Ether dissolves some of the colouring matter:

Natural colouring matter—

Annatto.

Turmeric.

Saffron.

Carotin.

Non-sulphonated acid coal-tar colors, such as

Aniline Yellow.

Butter Yellow.

Victoria Yellow.

Martius Yellow.

(2) Ether does not dissolve the colouring matter:

Basic coal-tar colours, such as—

Phosphine.

Sulphonated coal-tar colours, such as—

Acid Yellow.

Methyl Orange.

Orange IV.

Cheese.—The cheese, divided as finely as possible, is boiled with alcohol and the mixture filtered. The filtrate is evaporated to dryness on a steam bath and the residue treated as under (b) immediately above. The basic colours may be separated from the acid dyés as indicated on page 645.

Butter, Oils and Fats.—Butter colours and their detection have already been treated in Vol. II, page 308.

Martin (*Analyst*, **12**, 70) recommends that 2 parts of carbon disulphide should be gradually added, with gentle agitation, to 15 parts of alcohol or wood spirit. Five grm. of the butter to be tested, which need not be previously clarified, is shaken with 25 c.c. of the solution so obtained. On standing for a few minutes, the mixture separates into two layers, the lower of which is a solution of the fat in carbon disulphide, while the upper alcoholic stratum will be yellow if any artificial colouring matter be present. If the butter be but slightly coloured a larger amount should be employed. The alcoholic stratum will give a greenish colouration with nitric acid, and a red with hydrochloric acid and sugar if saffron be present. A brownish colour with ammonia indicates turmeric, and a blackish colouration with silver nitrate, marigold. If the alcoholic solution be evaporated to dryness, and the residue treated with concentrated sulphuric acid, annatto will be indicated by a greenish-blue, and saffron by a blue colouration. On adding a few drops of boric acid solution and again evaporating, turmeric will be indicated by a brownish-red colouration, changed to blue or green by alkali hydroxides. Dinitro-cresol and dinitro-napthol will be detected by treating the residue with ammonia, and adding excess of hydrochloric acid, when a light yellow crystalline precipitate will be formed, soluble in ether. The residue obtained by evaporating the ether solution, is soluble in alcohol, and after dilution with water the hot solution will dye fibres of silk or wool without a mordant.

Moore (*Analyst*, **11**, 163) has pointed out that when a butter coloured with carotin is dissolved in carbon disulphide and shaken with alcohol, as prescribed by Martin, the alcohol remains colourless, while the lower layer is deeply coloured; but on adding a drop of dilute solution of ferric chloride and again shaking, a gradual change is observed, the alcoholic layer becoming distinctly yellow and the carbon disulphite solution of the fats quite colourless, or retaining only the pale yellow colour due to the natural colouring matter of the butter. Excess of ferric chloride must be avoided. Leach (*Food Inspection and Analysis*, 1909) detects annatto by treating 2–3 grm. of the melted

and filtered fat with warm dilute sodium hydroxide. After stirring, the warm mixture is poured upon a wet filter using to advantage a hot funnel. If annatto is present the filter will absorb the colour, so that when the fat is washed off by a gentle stream of water the paper will be stained a straw colour. It is well to pass the warm alkaline filtrate 2 or 3 times through the fat on the filter to insure removal of the colour. If, after drying the filter the colour turns pink on application of a drop of stannous chloride solution, the presence of annatto is assured.

Some oil soluble coal-tar colours may be separated from the oil by saponifying the latter in the ordinary way and extracting the colour from the soap with ether.

Low (*J. Amer. Chem. Soc.*, 1898, **20**, 889) places a small amount of the melted fat in a test-tube and adds an equal volume of a mixture of 1 part of concentrated sulphuric acid and 4 parts of glacial acetic acid, and while shaking heats nearly to the b. p. On standing until the acid solution has settled out the latter in the presence of azo colours will be found to have acquired a wine-red colour. With pure butter fat comparatively no colour will be produced.

Annatto and *saffron* may be detected by Cornwall's method (*Bull.* 107 (revised), *Bur. Chem., U. S. Dept. Agr.*) 5 grm. of the fat are dissolved in 50 c.c. of ether in a separatory funnel and shaken vigorously with 12–15 c.c. of a very dilute solution of potassium hydroxide, which must still be alkaline after it separates from the ether solution. The mixture is allowed to stand a few hours, after which the aqueous layer is drawn off and evaporated to dryness. If the aqueous layer is not clear it sould not be filtered, since this removes large amounts of the colour, but it should be shaken with fresh portions of ether. Uncoloured butter treated in this way yields only slightly coloured residues. The dry residue is treated with concentrated sulphuric acid which in the presence of annatto produces a blue or violet-blue, changing quickly to green and finally to brown. Saffron acts similarly except that it does not give the green colouration. Vegetable colours in general impart a yellow tint to the alkaline solution when treated in the above manner.

Azo Dyes.—If 2 grm. of the filtered fat is dissolved in ether and shaken in a test-tube with 1–2 c.c. of dilute hydrochloric acid, the latter on separating will in the presence of some azo dyes be coloured pink or wine-red.

Cornelison (*J. Am. Chem. Soc.*, 1908, **30**, 1478) employs glacial acetic acid as a general reagent for detecting artificial colour in butter. About 10 grm. of the clear dry fat are melted and well shaken in a separatory funnel with 10–20 grm. of glacial acetic acid (99.5%). If the materials are too hot the fat will dissolve, but at about 35° it separates quickly and almost completely. The clear acid is drawn off, and after noting its colour it is tested by adding to 1 portion of 5 c.c. a few drops of concentrated nitric acid and to another portion a few drops of conc. sulphuric acid. The reactions are indicated in the following table:

Colouring matter	Colour of acid extract	Conc. HNO_3	Conc. H_2SO_4	H_2SO_4 and enough ether to clear solution
Pure natural butter (yellow).	Water white.....	Water white ...	Faint pink after a while.	Water white.
Soudan I........	Decided pink....	Strong pink....	Strong clear pink.	Pink.
Butter Yellow ...	Very faint pink.	Faint pink.....	Faint pink	Fain colour.
Cerasin Orange G. (Cassella)....	Greenish-yellow, strong.	Acid yellow, oil globule salmon-pink.	Same as with HNO_3.	Brownish-yel-yellow.
Yellow O. B. (H. & M.)	Bright yellow, not very strong.	Acid faint pink, oil globule salmon-pink.	Similar to HNO_3.	Pink.
Yellow A. B. (H. & M.	Warm ochre-yellow, weak.	Pink, fat colourless.	Brownish-pink, oil faint pink.	Pink.
Annatto.........	Dull yellow......	Little change...	Faint pink after a while.	Very faint yellow.
Curcumin........	Intense greenish-yellow.	Dull ochre-yellow.	Strong pink.....	Yellow.
Carrot...........	Very faint greenish yellow.	Faint yellow....	Faint pink after a while.	Very faint yellowish.
"Alderney butter colour" (H. & M.)	Brownish-yellow.	Strong pink....	Strong pink.....	
Ranson's butter colour ("vegetable").	Yellow..........	Almost decolourised.	Same as HNO_3.	
"Dandelion brand butter colour ("Vegetable").	Yellow..........	Almost decollourised.	Same as HNO_3.	

Aniline Yellow (amidoazobenzene) and butter yellow (dimethylaminoazobenzene) are extracted from oils by shaking the latter in a separatory funnel with about half their volume of 95% alcohol containing one-tenth its volume of concentrated hydrochloric acid. The alcohol layer is separated, diluted with an equal volume of water, and the small amount of oil that separates removed by shaking with light boiling petrolic ether. The alcohol layer is again separated, poured into a casserole, and solid sodium acetate added to it until the pink colour changes to yellow. A piece of wool is then introduced and the mixture boiled until the colour is fixed upon the wool. Butter Yellow

may be distinguished from Aniline Yellow by saturating a small piece of the dyed fibre in weak sodium nitrite solution and then treating it with dilute hydrochloric acid (10%). Butter yellow becomes pink or red, Aniline Yellow remains yellow.

Mathewson (*Proceedings A. O. A. C.*, 1910, *Bulletin* 137, *U. S. Dept. Agri., Bur. Chem.*) has published the following scheme for the separation and identification of oil soluble colours used in foods:

The colour is obtained in ether solution (see methods given above).

I. Shake the ether solution with 2% ammonium hydroxide. Ammonia solution coloured yellow.

Neutralize the alkaline extract, shake with ether, evaporate the ether, and add to the residue a few drops of alcohol and a little solution of stannous chloride in hydrochloric acid, or better a solution of titanium trichloride. Make strongly alkaline with sodium hydroxide, add water to make 15 to 20 c.c. and distill from a small flask until 7 to 10 c.c. are obtained. If oil is present in the reduced ammonia extract shake the alkaline mixture with ether, separate the ether and shake the latter with dilute hydrochloric acid. Add an excess of sodium hydroxide to the acid solution and distill. The distillate contains aniline—*Sudan G* (*A*) present.

II. Shake the ether solution from which the Sudan G has been removed, with 8% hydrochloric acid (1 volume concentrated hydrochloric acid and 4 volumes water).

(a) A violet-red colour is readily extracted.

The dye separated from the extract by neutralizing and shaking with ether and then evaporating the solvent gives a red colour in concentrated sulphuric acid. On reduction and distillation as under Sudan G, it yields aniline—*Benzene-azo-α-naphthylamine* present.

(b) A red colour is extracted with difficulty.

(1) Divide the acid extract into 2 parts. Nearly neutralise 1 part, cool to room temperature, add 1 drop of 5% sodium nitrite solution and allow to stand for a few minutes. Pour the mixture into 15 c.c. of 5% sodium carbonate solution to which has been added a few drops of 1% beta-naphthol solution. If a red colour (due to formation of Sudan III) is produced, shake the mixture with ether, wash the ether solution, evaporate the solvent and test the residue with 85 to 90% by volume sulphuric acid. An intense green colour is produced—*Aniline Yellow* present.

(2) Reduce the second portion of the acid extract with a solution of stannous chloride or better titanium trichloride. Add an excess of

sodium hydroxide and shake with ether. Wash the ether layer with water and then shake with 5 to 8 c.c. of dilute (N/5) hydrochloric acid. Draw off the acid solution and add to it a drop or two or 0.2% ferric chloride solution. An intense rose colour changing to blue appears—*Butter Yellow* is present.

III. Shake the ether solution from which the preceding dyes have been extracted, with 12% hydrochloric acid (1 volume concentrated hydrochloric acid and 2 volumes water). Neutralise the acid extract, shake the colour into ether, separate and evaporate the ether layer, and reduce and distill the residue as given under sudan G. The distillate yields α-naphthylamine—*Amino-azo-α-naphthaline* present.

IV. Shake the ether solution from which the preceding colours have been removed with 5 % potassium hydroxide solution.

(a) A brownish-red colour is readily extracted.

On reduction and distillation as under Sudan G, it yields aniline —*Benzene-azo-α-naphthol* present.

(b) A deep red colour is extracted with difficulty.

(1) On reduction and distillation as under Sudan G it yields α-naphthylamine—*Sudan Brown* (*A*) present.

(2) On reduction and distillation as under Sudan G it yields β-naphthylamine—*Beta-naphthalene-azo-α-naphthol* present.

V. The ether solution from which the preceding colours have been removed is still deeply coloured.

Evaporate, add a little alcohol, reduce with stannous chloride and hydrochloric acid, make alkaline and distill as under Sudan G.

(a) Distillate yields aniline.

(1) A little of the unreduced dry residue from ether solution (V) gives a green solution in concentrated sulphuric acid—*Sudan* III (*A*) present.

(2) A little of the unreduced dry residue from ether solution (V) gives a red solution in concentrated sulphuric acid—*Sudan I* (*A*) present. Sudan I is also much more soluble in concentrated hydrochloric acid and in alcohol than Sudan III.

(b) Distillate yields xylidine—*Sudan II* (*A*) present.

(c) Distillate yields α-naphthylamine—*Carminaph Garnet* (*D. H.*) present. (If Sudan Brown was present it must be completely extracted before testing for Carminaph Garnet. This extraction is somewhat difficult.)

Identification of the Amines in Distillates. β-naphthylamine.—Shake a portion of the distillate with ether and evaporate the ether with a trace of furfurol (conveniently in ether solution also). β-naph-

thylamine gives an intense purple, α-naphthylamine a yellowish-red, and aniline a crimson residue.

α-**Naphthylamine.**—Treat a mixture of a few decigrms. of sulphanilic acid in about 50 c.c. of water with 2 drops of concentrated hydrochloric acid and 2 to 3 drops of 5% sodium nitrite solution, the sulphanilic acid remaining in excess. Add some of this solution to a portion of the distillate. If α-naphthylamine is present an intense rose colour appears at once. β-naphthylamine gives a much less marked orange colour or turbidity. Aniline and its homologues give no colouration. If aniline be substituted for sulphanilic acid in making the test α-naphthylamine gives an intense rose colour, α-naphthylamine (in the absence of α-naphthylamine) a greenish-brown colouration or turbidity.

Aniline and Homologues.—Allow the mixture of distillate with diazotised sulphanilic acid (see above) to stand for 10 minutes, then make alkaline with potassium hydroxide and shake with ether which will take up aniline and its homologues if present. Wash the ether, shake with very dilute hydrochloric acid, separate the aqueous layer and add to it one drop of 5% sodium nitrite solution. Pour the resulting diazo solution into an excess of 5% sodium carbonate to which has been added a few drops of 10% β-naphthol. A red colour or turbidity indicates the presence of aniline or its homologues. Make the solution alkaline with sodium hydroxide, shake with ether and wash the ether solution with water. Pour into a test-tube and evaporate off the ether. Add to the residue 3 to 4 c.c. of concentrated hydrochloric acid, heat to boiling and add one drop of concentrated nitric acid to the solution. With the amounts ordinarily present xylene-azo-β-naphthol (Sudan II) from xylidine gives a clear yellow colour and benzene-azo-β-naphthol (Sudan I) an orange turbidity. The test can of course be applied directly to mixtures of the sudans to detect Sudan I.

The amine solution may also be tested with lead peroxide and acetic acid (Lauthe's test). It should be strongly acid with acetic acid and contain the amine in such dilution that no colouration appears until the mixture has stood some moments. Under these conditions xylidine gives a purple colour, aniline a brown passing to red.

COLOURS OF SOLUTIONS OF DYES IN CONCENTRATED SULPHURIC ACID.

Aniline-yellow—Yellow.
Butter-yellow—Yellow.
Benzene-azo-α-naphthylamine—Orange-red.
Amino-azo-α-naphthaline—Blue.
Sudan I (A)—Cherry-red.
Sudan II (A)—Violet-red.
Sudan G (A)—Yellowish-brown.
Benzene-azo-α-naphthol—Violet.
Sudan brown (A)—Greenish-blue.
β-naphthaline-azo-α-naphthol—Violet-blue.
Carminaph garnet (D. H.)—Bluish-violet.
Sudan III (A)—Green.

INKS.

By PERCY H. WALKER, M. S.

WRITING INKS.

Writing inks are either coloured liquids, or liquids containing a finely-divided precipitate in suspension.

Ordinary writing ink was formerly always made from a decoction of galls, to which copperas was added. Of late, the composition of writing inks has become far less constant, aniline and other dyes being frequently employed, and other metallic salts substituted for the ferrous sulphate formerly invariably used.

The best black ink is a tanno-gallate of iron, obtained by adding an infusion of nut-galls to a solution of ferrous sulphate (copperas). The galls contain gallic and gallotannic acids, both of which are serviceable. On coming in contact with ferrous salts in concentrated solutions, these produce white precipitates which turn black on exposure to air. With ferric salts, blue-black precipitates are at once produced. A small quantity of gum is added to retain the precipitate in suspension. To ink intended for copying by pressure a small addition of sugar or glycerine is also made.

Sumac is sometimes used instead of galls, and some of the nut-gall inks contain a little acetic acid, added as vinegar.

Some of the gallic inks receive an addition of indigo-carmine or indigo disulphonic acid. Aniline dyes are frequently used as a whole or part of the colouring matter of both black and coloured inks.

Other black inks can be made from extract of logwood; with salts of iron the ink is greenish, changing to black on drying; with salts of aluminum, violet-black, and with potassium chromate, black. Ammonium vanadate forms a black ink with gallotannic acid. This type of ink is frequently stated to be very permanent, but this statement is not correct. Various aniline colours such as nigrosine have been used in making black inks. The logwood, chromium, vanadium and aniline dye black inks are not resistant to light and are not suitable for use as

record inks. Carbon inks such as India or Chinese ink are composed of lampblack mixed with glue. Liquid carbon inks are made by incorporating lampblack in solutions of gluten, alkaline solutions of shellac, or other suitable liquids. These carbon inks are not affected by light or chemicals, but they do not generally flow readily from the pen and can be removed mechanically from the paper. They are used as drawing inks, but not to any extent as writing inks. It is therefore safe to assume that the best record black inks are iron gallotannic inks.

Coloured inks do not usually contain tannic acid; in many instances they are nothing but solutions of coal-tar dyes. The following examples will suffice to give a general idea of their composition:

Red.—Brazil wood, with stannous chloride or cream of tartar and alum; cochineal or carmine dissolved in ammonia or sodium silicate; eosine. There is no permanent red ink.

Blue.—Prussian blue dissolved in oxalic acid (permanent); Aniline Blue.

Violet.—Aniline Violet.

Green.—Acetate of copper and cream of tartar; Diamond Green.

Marking inks are all closely analogous in composition, and their assay requires no special description. They usually consist of nitrate of silver coloured with sap-green, ivory-black, indigo, etc.; or ammonio-nitrate of silver mixed with sodium carbonate, sometimes with sulphate of copper added. In Redwood's ink, tartrate of silver is substituted for the nitrate. Reade's ink is ammonio-tartrate of silver.

Printing ink is made by suspending lampblack or other pigment in linseed oil, with more or less rosin oil, rosin, turpentine, etc. Stamping ink, for use with metal stamps, is similar to printing ink; that for use with rubber stamps is made up without oil, the vehicle being glycerin to which alcohol is sometimes added.

Invisible inks are such that give visible characters only after a chemical treatment of the writing. A solution of lead acetate may be used for this purpose, when the writing will become visible on exposure to vapours of hydrogen sulphide. Potassium ferrocyanide solution will give a writing which can be developed by moistening with a dilute solution of an iron salt. A writing which will fade away can be made by using an ink prepared from rice starch, water, and a few drops of tincture of iodine. The writing may be restored by exposing to the vapor of iodine.

The following estimations are of value in examining a black writing ink:

For the detection of *organic colouring matters*, a portion of the ink should be strongly acidified with hydrochloric acid. A blue colour, unaffected by the acid, but destroyed on adding bromine water or bleaching powder, shows the presence of indigo. If Prussian blue be present, the ink will probably turn brown on addition of sodium hydroxide, and the filtered liquid will give a deep blue precipitate with ferric chloride, after being acidified with hydrochloric acid. A black colour, not destroyed by acids or alkalies, nor bleached by chlorine or bromine, is pretty certain to be due to finely-divided carbon. An ink prepared with ammonium vanadate and galls is turned blue by acids, but is unaffected by alkalies. Its colour is altered but not bleached by chlorine. Aniline-black is not affected by alkalies, but is turned dark green by acids; bleaching powder renders it garnet-red. Logwood inks are turned red or yellow by hydrochloric acid, while those containing galls only are almost wholly decolourised by the same reagent.

Sp. Gr.[1]—Determine with a pyknometer at 15.6°.

Total Solids.[1]—Weigh 10 grm. of ink in a flat-bottomed platinum or porcelain dish, evaporate to dryness on the water-bath, and then heat in an oven at the temperature of boiling water for 2 hours; cool in a desiccator and weigh.

Ash.[1]—Burn the residue from the estimation of total solids at a low temperature, preferably in a muffle. In order to avoid loss by foaming the dish used should not be too small, not less than 50 c.c. capacity.

Iron.[1]—Transfer the ash to a small beaker and dissolve in 15 c.c. of hydrochloric acid with the addition of stannous chloride at the temperature of the steam bath; reduce by adding stannous chloride, drop by drop, to the hot solution until the colour is destroyed, and then add 1 or 2 drops in excess. Wash the reduced iron solution from the small beaker into a 600 c.c. beaker and dilute to about 250 c.c. with cold water, add all at once an excess of mercuric chloride, stir, allow to stand a minute, and titrate with standard potassium dichromate solution.

Sulphuric Anhydride (SO_3).[1]—Estimate both iron and sulphuric anhydride in the same sample. Place from 10 to 15 grm. of ink in a platinum dish, add 1 to 1.5 grm. of sodium carbonate previously dissolved in water, evaporate to dryness, ash, extract with water, add

[1] Bulletin 109, Revised, Bureau of Chemistry, U. S. Department of Agriculture.

bromine water to the extract, boil, render acid with hydrochloric acid, boil off the bromine and determine the sulphuric anhydride (SO_3) by precipitation with barium chloride. Dissolve the insoluble residue in hydrochloric acid and estimate iron as described in the preceding section. Or, in case the small amount of platinum (which always goes into solution when iron oxide is dissolved by hydrochloric acid in platinum) causes trouble with the potassium dichromate method, add sulphuric acid, evaporate to fumes, dilute, reduce with zinc, and titrate with potassium permanganate.

Chromium.—Chromium is not a common constituent in a good black ink, but when present it can be estimated in the ash by fusing in a nickel crucible with sodium carbonate and sodium peroxide to oxidise to chromate, dissolving in water and boiling to expel thoroughly all hydrogen peroxide, cooling, rendering acid with sulphuric acid, adding a measured amount of standard ferrous sulphate and titrating the excess of iron with standard potassium dichromate.

Keeping in Ink Wells.[1]—Allow the bottle of ink sample to stand perfectly still at room temperature for 3 days. Carefully remove the stopper without shaking the bottle and draw out about 50 c.c. with a pipette from the middle of the bottle. Filter this through a dry quantitative filter-paper, exposing it as little as possible to the air, and of the filtrate take 25 c.c. in a clear glass bottle (140 mm. high, 56 mm. in diameter, with a neck 32 mm. in diameter); an 8-oz. salt-mouth bottle answers the purpose. Cover the top of the bottle with a piece of filter-paper, using a small amount of mucilage or paste to stick the paper firmly across the neck. Keep at room temperature and in ordinary daylight in a room free from acid or ammonia fumes. Let stand for 14 days, noting from day to day whether any mould or film forms on the surface and whether any sediment forms on the walls or bottom of the bottle.

Action on Steel Pens.—Immerse steel pens in the ink and leave them there for 7 days. Remove the pens each day, clean them, and note whether the metal appears corroded; also note whether the ink becomes thick. When much corrosion takes place it may be advisable to weigh the cleaned pens each day.

Streak Tests.[1]—Procure a supply of uniform, good quality, medium weight, all-rag writing-paper in sheets 265x200 mm. Stretch a sheet of this paper on a smooth board inclined at an angle of 45° and let

[1] Bulletin 109, Revised, Bureau of Chemistry, U. S. Department of Agriculture.

flow from a tube, held vertically near the top edge of the paper, 0.6 c.c. of the ink. For this purpose use a tube 250 mm. long with a bore of about 3.5 mm. and a mark 62 mm. from the lower end. By drawing the ink up to the mark and allowing what will to flow out across the paper uniform streaks can be made. Make streaks with the undiluted inks and with the inks diluted with an equal volume of water. Allow to dry and note the penetration, stickiness, and fluidity of the different streaks. The ink should penetrate into the fibres of the paper but not pass through. The streaks should not be sticky. By carefully making the streaks and comparing, a very good idea of the fluidity can be formed. A normal ink should give an oval head to the streak and the rest should be nearly uniform in width; a very fluid ink forms a streak with wide head which rapidly narrows down.

Resistance to Sunlight and Reagents.[1]—Cut the sheets of streaked paper into strips about 4 cm. wide, cutting at right angles to the streaks. With a lead pencil place identification marks near each streak. Cover half of some of the strips with black paper, clamp under glass in a photograph frame, and expose to sunlight. Keep the remaining strips in diffused daylight in an atmosphere free from acid or ammonia fumes for 8 days. Expose some of these last strips to the weather uncovered, using some for tests with reagents and reserving others for final comparisons. If the ink is a copying ink, make press copies of some of the strips as soon as they are thoroughly dry and treat the press copies and the copied original like the other strips. Immerse the strips in the reagents used for testing them and observe the effect at the end of 15 minutes, 1 hour, and 24 hours. The following reagents are used, though of course others may be added: (1) Water; (2) alcohol (95%); (3) 90 volumes of water and 10 volumes of ammonia (0.90 sp. gr.); (4) 90 volumes of 95% alcohol and 10 volumes of ammonia (0.90 sp. gr.); (5) hydrochloric acid (2%); (6) sodium hydroxide (2%); (7) bleaching powder solution (N/200 available chlorine). (See insert.)

The exposure to sunlight should extend over a period of at least 14 days and if possible longer.

Standard Ink.

Since no ink is wholly resistant to reagents and sunlight, it is necessary to have a standard for comparison. The standard record ink,

[1] *Bulletin* 109, *Revised, Bureau of Chemistry, U. S. Department of Agriculture.*

originally adopted by the Prussian gbvernment, has been practically adopted by the state of Massachusetts and by the United States government. The specification for record ink for the state of Massachusetts is as follows:

The ink should have the properties of flowing freely from the pen and making a legible and permanent record. It must be a gallate and gallo-tannate of iron ink, not inferior in any essential quality to one properly prepared after the following formula, in which all the ingredients are of the quality prescribed by the United States Pharmacopœia, and the percentage of true acid present in the sample of tannic acid used has been determined by the Loewenthal and Schroeder method: Pure, dry tannic acid, 23.4 parts, by weight; crystal gallic acid, 7.7 parts; ferrous sulphate, 30.0 parts; gum arabic, 10.0 parts; diluted hydrochloric acid, 25.0 parts; carbolic acid (C. P.), 1.0 part; and water, sufficient to make up the mixture at the temperature of 15.5°, to the volume of 1,000 parts by weight of water.

Inks submitted will be subjected to the following tests as compared with the standard ink described above:

1. A fluid ounce allowed to stand at rest in a white glass vessel freely exposed, in diffused daylight, for 2 weeks to the light and air at a temperature of 10° to 15.5°, protected against the entrance of dust, must remain as free from deposit upon the surface of the ink or on the bottom or sides of the vessel.

2. It must contain no less iron.

3. It must give as quickly, and after a week's exposure to diffused daylight, as intense a black colour when used upon the standard record paper; and the marks must equally resist changes from light, air, water or alcohol.

4. It must be as fluid, flow as well, strike no more than through the paper, nor remain more sticky immediately after drying.

An ink made in accordance with this formula should have a sp. gr. of 1.036, and should contain not less than 0.60% of iron.

In preparing this standard ink dissolve the tannin and gallic acid together in about 50 parts of warm water, the ferrous sulphate in about 150 parts of cold water, and the gum arabic in about 150 parts of warm water. Allow the warm solutions to cool, add the hydrochloric acid to the ferrous sulphate, and immediately mix all the solutions, and make up to 1,000 parts with distilled water. Mix thoroughly and allow to stand for a least 4 days at room temperature. Without

Serial number.	Sp. gr. 15.5°	Total solids %.	Ash %.	Iron %		e of water. it. 80 days.
1721	1.0273	4.13	1.23	0.37		very badly.
1960	1.0264	4.14	1.08	0.35		badly.
1962	1.0207	3.22	0.62	0.38		badly.
1330	1.0205	3.06	0.61	0.33		very badly.
1717	1.0207	3.28	0.62	0.32		badly.
1718	1.0395	6.50	1.17	0.65		ange.
1850	1.0363	5.95	1.08	0.60		ange.
1982	1.0367	6.04	1.05	0.67		badly.
1720	1.0473	7.63	1.39	0.73		ange.
1964	1.0473	7.43	1.40	0.80		ange.
1985	1.0493	7.95	1.41	0.79		ange.
1851	1.0887	13.84	2.65	1.46		ange.
1986	1.1093	16.87	3.01	1.80		ange.
1965	1.0634	11.20	3.91	0.06	$K_2Cr_2O_7$	badly.
1432	1.0069	1.36	0.18	0.05		completely.
1433	1.0209	3.48	0.67	0.26		very badly.
1434	1.0182	2.81	0.50	0.27		very badly.
1981	1.0068	1.26	0.17	0.14		completely.
1961	1.0377	6.21	1.20	0.68		slightly.
1729	1.0175	2.71	0.58	0.23		completely.
1984	1.0204	3.17	0.59	0.31		badly.
1722	1.0169	3.01	0.85	0.73	$K_2Cr_2O_7$	almost complete
1725	1.0169	3.00	0.86	0.74	$K_2Cr_2O_7$	almost complete
1329	1.0185	3.36	0.85	0.14		very badly.
1727	1.0411	7.15	1.18	0.50		very badly.
1732	1.0160	2.76	0.80	0.16		almost complete
1963	1.0204	3.42	0.88	0.19		very badly.
1723	1.0120	1.97	0.55	0.14		almost complete
1730	1.0099	1.72	0.45	0.12		completely.
1431	1.0377	7.43	0.88	0.32		ange.

shaking the bottle draw out the ink to be used in making comparisons. This standard ink will not be of a good colour, but will make a dirty grey-green mark which will finally turn black. Schluttig and Neumann (Die Eisingallustintien) recommend colouring the standard ink to match the ink to be tested by the addition of soluble coal-tar dyes.

Ratings of a number of samples of ink are entirely relative and of course any system may be adopted. For record inks the exposure to sunlight is the most important test and the following scheme is used in the Bureau of Chemistry, U. S. Department of Agriculture, for rating a standard ink:

Exposure to sunlight	70
Exposure to reagents	10
Keeping quality, penetration, stickiness, fluidity, and action on steel pens	15
Composition	5
Total	100

Other record inks are given values above or below the figures for the standard ink, as the judgment of the analyst may indicate; thus the total for a very good ink may be over 100.

L. S. Munson[1] made an examination of 30 samples of ink representing 18 distinct brands and the products of nearly all the large manufacturers in the United States. 27 of the samples were iron-tannin inks and 3 were chromate logwood inks. The results of this examination are shown in the following table:

Chemical Examination of Ink Marks.

In chemico-legal cases it is sometimes of importance to ascertain the nature of the ink used, to compare it with specimens of writing of known history, and to ascertain the relative ages of the writings. A minute inspection should first be made with a magnifying power of about 10 diameters, and any peculiarities of colour, lustre, shade, etc., duly noted, and where lines cross each other which lie uppermost. The examination is often facilitated by moistening the paper with benzene or petroleum spirit, whereby it is rendered semi-transparent. The use of alcohol or water is inadmissible.

Valuable information is often obtainable by treating writing or

[1] *J. Amer. Chem. Soc.* 1906, 28.

other ink-marks with reagents. Some inks are affected much more rapidly than others, though the rate of change depends greatly on the age of the writing. Normal oxalic acid (63 grm. per litre), or hydrochloric acid of corresponding strength, should be applied to a part of the ink marked with a feather or camelhair brush (or the writing may be traced over with a quill pen), and the action observed by means of a lens, the reagent being allowed to dry on the paper.[1] Recent writing (1 or 2 days old) in gallic inks is changed by 1 application of oxalic acid to a light grey, or by hydrochloric acid to yellow. Older stains resist longer, in proportion to their age, and a deeper colour remains. Logwood ink marks are mostly reddened by oxalic acid, and alizarin marks become bluish, but aniline inks are unaffected. With hydrochloric acid, logwood ink marks turn reddish or reddish-grey, alizarin marks greenish, and aniline ink marks reddish or brownish-grey. The treatment with acid should be followed by exposure to ammonia vapours, or blotting-paper wet with ammonia may be applied. Thus treated, marks in logwood ink turn dark violet or violet-black. The age of ink marks very greatly affects the rate of their fading when treated with dilute ammonia, the old marks being more refractory. The behaviour of ink marks when treated with solution of bleaching powder is often characteristic, the older writings resisting longer; but unless the reagent be extremely dilute, writings of all ages are removed almost simultaneously (R. Irvine, *Jour. Soc. Chem. Ind.*, **6**, 807). Hydrogen peroxide acts more slowly than bleaching solution, but gives more definite results. After bleaching the marks by either reagent, the iron of the ink remains mordanted on the paper, and the mark may be restored by treatment with a dilute solution of galls, tannic acid, or acidified potassium ferrocyanide. The same reagents may be used for restoring writing which has faded from age alone.

When ink marks have been erased or discharged by chemical means, traces of the treatment are often recognisable. After effecting the erasure, the spot is often rubbed over with powdered alum or gum sandarac, or coated with gelatin or size. The bleaching agents most likely to have been used are oxalic, citric, or hydrochloric acid, bleaching powder solution, or acid sulphite of sodium. Moistened litmus paper will indicate the presence of a free acid, and in some cases treat-

[1] Allen succeeded by this treatment in detecting an alteration in a receipt on account in which a figure 1 had been altered to 4. The added mark, as also a forged signature across the stamp necessitated by the change, faded out first under treatment with dilute hydrochloric acid.

ment with ammonia fumes will restore the colour. The presence of calcium, chlorides, or sulphates in the water in which the paper is soaked will afford some indication of bleaching powder or a sulphite having been used. Potassium ferrocyanide will detect any iron remaining in the paper. Exposure to iodine vapour often affords evidence of chemical treatment, and other methods of examination readily suggest themselves.

The application of reagents to writing in black ink has been recommended by W. Thomson for the identification of handwriting (*Chem. News*, **42**, 32).

Robertson and Hoffmann (*Pharm. Centr.*, **33**, 225) propose a treatment of written characters with the following reagents in order to detect forgeries and alterations:

1. 3% solution of oxalic acid in water.
2. 10% solution of citric acid in water.
3. 2% solution of chloride of lime in water.
4. Solution of 1 part stannous chloride in 1 part of hydrochloric acid and 10 parts of water.
5. 15% sulphuric acid solution.
6. 10% hydrochloric acid solution.
7. 20% nitric acid solution.
8. Saturated solution of sulphur dioxide in water.
9. 4% solution of gold chloride in water.
10. Solution of 1 part potassium ferrocyanide in 1 part of hydrochloric acid and 10 parts water.
11. Solution of 1 part sodium thiosulphate in 1 part ammonia and 10 parts water.
12. 4% solution of sodium hydroxide.

These reagents should be applied by means of a quill pen drawn over the characters. Their action on a number of different inks is given in the following table. The reactions should be observed under a power of 100 diameters.

When characters have been removed by other than chemical means, proof may be obtained by means of a photograph taken by transmitted light, or by exposing the paper to iodine vapour. The latter process is especially useful in cases where, for the removal of the writing, the paper has been moistened; these places become blue, the other brown. When the removal has been effected by chemical means, in most cases by oxalic acid, chloride of lime and sulphur dioxide, the suspected

Reagents	Iron gallotannic ink	Logwood		Nigrosin	Vanadium ink	Resorcin ink
		With potassium chromate	With copper sulphate			
Oxalic acid.	Disappears.	Violet.	Orange-yellow.	Unchanged.	Fades, and runs a little.	Bright red.
Citric acid.	Fades.	Violet.	Orange-yellow.	Runs, with dark blue colour.	Fades and runs.	Disappears.
Hydrochloric acid.	Disappears, but leaves behind a yellow colouration.	Purplish-red.	Blood-red.	Slightly altered.	Fades slightly and runs a little.	Bright pink.
Sulphuric acid.	Disappears.	Red.	Purplish-red.	Unchanged.	Fades a little.	Bright red.
Nitric acid.	Disappears.	Red.	Purplish-red.	Runs a little.	Fades a little.	Bright pink.
Stannous chloride.	Disappears.	Red.	Magenta-red.	Unchanged.	Fades a little.	Disappears.
Sulphurous acid.	Fades.	Greyish-violet.	Red.	Unchanged.	Fades a little and runs.	Fades.
Gold chloride.	Fades slightly.	Reddish-brown	Brown.	Unchanged.	Unchanged.	Runs, with brown colour.
Sodium thiosulphate and ammonia.	Dark red.	Unchanged.	Dark blue.	Dark violet, runs.	Runs very much.	Brown.
Potassium ferrocyanide and hydrochloric acid.	Blue.	Red.	Brick-red.	Unchanged.	Unchanged.	Pink.
Sodium hydroxide.	Dark red.	Brown.	Dark red, runs.	Dark violet, runs.	Dirty brown, runs.	Unchanged.
Chloride of lime.	Disappears.	Disappears.	Disappears, but leaves a yellow colouration.	Brown.	Unchanged.	Brown.

places are treated with a solution of sulphur dioxide in water, then with 3% solution of hydrogen peroxide, and finally with dilute ammonia. After the evaporation of the excess of ammonia, good results may be obtained with tannin, which darkens the characters.

Cancelling Inks having an Oil Base.[1]

The following methods have been devised for the purpose of ascertaining the suitability of cancelling inks for the use of the Post-Office Department, U. S. A, Many of these methods will be found of assistance in passing upon the quality of stamping inks for miscellaneous uses.

It is important that the ink used by the Post-Office Department for post-marking possess in the highest possible degree certain properties. The ink, first of all, must produce an indelible cancellation; that is, it must be relatively indelible as compared with the ink used for printing the postage stamps. The postmark made with the ink must dry quickly in order that the mail matter may be handled immediately without any blurring or smearing of the postmark. Both this property and the property of indelibility involve the question of the rate at which the ink penetrates or is absorbed by the fibre of the paper. A satisfactory ink does not harden or form a crust on the ink pad on exposure to the air. There must be no deposition of solid matter on the bottom of the vessel in which the ink is stored, and the pigments, on which the indelibility of the ink depends, if insoluble, must not settle out in such a way as to make it possible to pour off from the top of the container a portion of the ink which contains little or none of the insoluble pigment or pigments. The following methods have been found of value for the purpose of ascertaining the quality of a given sample of ink as well as the appropriateness of certain materials used for the manufacture of cancelling inks.

1. **Preparation and Care of the Sample.**—Since cancelling inks contain more or less insoluble and volatile matter, special attention must be given to the preparation and care of the sample. It must be carefully mixed by shaking before each portion is removed for analysis, and the container must be left open no more than is absolutely necessary for the removal of portions of the ink.

2. **Estimation of Matter Volatile at Ordinary Temperatures.**—

[1] *Bulletin* 109, *Revised, Bureau of Chemistry, U. S. Department of Agriculture.*

Place a carefully weighed quantity (between 5 and 5.2 grm.) of the ink in a flat-bottomed aluminum dish 102 mm. (4 inches) in diameter. Distribute the ink completely over the surface of the bottom of the dish by gently tilting the same. This quantity of ink should be sufficient to completely cover the bottom of the dish. Place the dish on a horizontal shelf or table where air will have free access to it and where it will be screened in such a way that no dust can fall into it.

Re-weigh the dish at the end of 18 hours, 24 hours, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 14 days, 21 days, and 28 days. Calculate the total percentage loss of weight at the end of each period of drying. The loss of weight should be gradual and should not exceed 15% during the first 7 days, nor 25% during 28 days. This test shows the absence of highly volatile ingredients and the absence of an excess of matter volatile at the ordinary room temperature. The constituents of a canceling ink should be such that the volatile matter will not exceed the above limits when the ink is exposed under the conditions named to a summer temperature of 26.6° (80° F.) and upward.

3. **Estimation of Relative Penetrating Power.—(a) Apparatus.**

(*a*) Homæopathic shell vials about 6 cm. long and 2 to 2.5 cm. in diameter.

(*b*) Strips of white blotting paper, which for a given series of determinations should be cut from the same sheet and of exactly the same dimensions. A convenient size is 12 mm. wide and 25 cm. long.

(*c*) A pair of dividers with arms 15 cm. long or longer.

(*d*) A millimetre rule.

(b) Estimation.

Place approximately 5 c.c. of the ink or other material to be tested in one of the "shell vials" described, and if several samples are to be tested arrange the vials in a row. Place 5 c.c. portions of distilled water in each of 2 of the vials, and put one of the vials containing water at each end of the row of vials containing samples to be tested. Proceeding from left to right, insert a strip of blotting-paper in each of the vials, recording the exact time the paper was placed in each vial. The blotting-paper should maintain a nearly upright position. The liquids gradually ascend the strips by capillarity; the strips, however, should be in such a position that the liquid does not ascend by capillarity between the edges of the strips and the sides of the vials.

At the expiration of exactly 15 minutes from the time each strip is inserted in the vial, measure the height to which the liquid has ascended the strip of paper by means of a pair of dividers and record the distance in millimetres. Make a second set of readings at the end of 45 minutes.

After all of the measurements have been recorded reduce the results to the terms of the penetrating power of distilled water, taking the penetrating power of distilled water as 100. This is accomplished by dividing each result by the average of the results obtained for the distilled water contained in the vials and multiplying the quotient by 100. 10 samples may conveniently be tested at one time by working as described. The method gives good comparative results, and has been applied not only to cancelling and other stamping inks, but to the liquids used for the manufacture of these inks.

In observing the penetrating power of a given sample of ink it is important to remember that the value of a cancelling or stamping ink depends upon its power to penetrate the paper during the first minute or fraction of a minute following its application to the paper. It is well, however, to keep the tests under observation for several hours, as information can thus be obtained in regard to the extent to which the colouring matter contained in the ink follows the liquid base of the ink as it passes through the paper. In some cases the colouring matters keep pace with the liquid portions of the ink; in others an uncoloured band at the top of the portion of the paper which is wet with the ink shows that the colouring matter does not proceed through the paper as rapidly as the base of the ink. This may or may not be an undesirable result. If the colourless band is due to a difference in the rate of penetration, it is undesirable. If it shows that the dye contained in the ink has an affinity for the fibres of the paper, it is evidence of a valuable quality.

Additional information can be obtained from the penetration test by removing the strips of paper from the vials, cutting off the part of the paper which has actually been immersed in the ink, and treating the upper part successively with petroleum, ether, alcohol, and other solvents for removal of the constituents of the ink soluble in these liquids. The extent to which the dye or dyes contained in the ink resist the action of these solvents and the extent to which the lampblack has passed up the strip of blotting paper are indices of the quality of the ink.

An examination of the strips with the microscope will give valuable information regarding the rise of carbon in the paper and the affinity

of the dye for the fibres of the paper. With many inks the carbon will not rise above the surface of the liquid, while with others it penetrates the paper to the same height as the dye. With this class of inks it is important that the base of the ink have the power to carry the carbon well into the fibres of the paper.

To make the determination allow the strips to remain in position until the next day, remove, dry between blotters, and examine for a rise of dye or carbon. If either dye or carbon rises as far, or nearly as far, as the base of the ink the rise is pronounced "satisfactory." Less than this is not acceptable except in the case of glycerine inks, which rarely give any rise of carbon. A small amount of rise in the latter inks must be accepted as satisfactory. To determine whether the rise is carbon or simply dye, pick off particles of the paper and adhering ink at intervals on the strip and mount on slides with water or alcohol. Examine with the microscope, using low power; note size of the carbon grains. The grains adhere to the outside of the paper fibres in clots, as a rule. It is often difficult to distinguish the carbon grains.

4. **Sedimentation Test.** **(a) Apparatus.**—(1) Glass-stoppered cylinders, graduated for 200 c.c. and fractions thereof, the distance between the bottom and the 200 c.c. mark being 25 cm. (10 inches). If unobtainable, other cylinders may be substituted, marks being placed at distances 25 cm. (10 inches) and 16 mm. (10/16 inch) from the bottom.

(2) A pair of dividers with arms 15 cm. long or longer.

(3) A millimetre rule.

(4) Pipettes made from straight tubing (7 mm.), at least 30 cm. in length and having a capacity of from 10 to 15 c.c.

(b) Estimation.—By means of the special pipette introduce carefully, drop by drop, into one of the 200 c.c. cylinders, exactly 16 mm. depth of the ink to be tested. The ink should be previously tested to determine a proper solvent for both base and dye. Alcohol is generally the solvent to use for rosin inks. It may be necessary to use other solvents, such as gasoline (b. p., 50° to 60°), ether, benzol, etc. Dissolve the ink in the cylinder in the appropriate solvent and dilute up to the 200 c.c. mark, stopper, and shake thoroughly. Allow the cylinder to stand, and record from time to time, by using the dividers and millimetre rule, the height of the top of the layer of sediment which collects in the bottom of the cylinder, expressing results in millimetres. During the first hour observations should be made at intervals of 15 minutes;

later, each hour for several hours successively, and then twice daily for a week to 10 days.

After the settling of the top of the layer of sediment has entirely ceased, the height of the sediment should equal or exceed 16 mm., the amount of ink taken for the test. The rate of sedimentation is an index of the state of division of the carbon, some inks showing no appreciable layer at the expiration of a 10-day test.

In the case of some inks the supernatant liquid above the sediment is of such a dark colour that there is difficulty in locating the top of the sediment, even when the cylinder is inspected by light reflected at various angles. In this event, the use of a dark room with a light placed so as to give a strong ray through a small aperture will locate the top of the layer of sediment in all cases except when the ink contains a very large percentage of a dense dye.

Frequently the layer may be located by holding an incandescent electric light at the back of the cylinder and noting where the carbon filament cannot be seen. The test is somewhat crude and only approximate, but it serves to give an idea of the fineness and amount of carbon, and, as a rule, agrees fairly well with the carbon determinations.

5. **Estimation of Lampblack.**—Load a porcelain gooch with asbestos, using a felt about ¼ inch thick. After washing the felt thoroughly with water to remove fine particles, finally wash with alcohol and ether, dry, and weigh. Weigh out about 5 grm. of ink in a small beaker, dilute with a suitable solvent (alcohol is used in case of rosin-oil inks), transfer to a Gooch crucible, and wash until all oil and soluble colour is removed. Finally, wash with alcohol and ether, dry, and weigh.

No one solvent can be used for all oil base inks. The analyst should determine the most suitable solvent by tests on separate portions of the ink in question. Filtering on a Gooch crucible is sometimes very tedious, and better results may frequently be obtained by mixing a weighed quantity of the ink in a suitable tube with the solvent, and settling out the pigment by whirling in a centrifugal machine. By pouring off the clear solvent and repeating the extractions, the solid pigment may be finally collected in the tube in which it is weighed after evaporating off the small amount of solvent which cannot be decanted.

6. **Estimation of Ash.**—The lampblacks prepared for the manufacture of cancelling ink yield less than 0.5% of ash when burned, and the coal tar dyes employed should contain no mineral matter other

than that which is an essential part of the molecules of the substances to which the tinctorial power of these dyes is due.

For the estimation of the ash, place 2 to 3 grm. of the ink in a porcelain dish, which must be of such size as to avoid loss of ink due to the foaming which is likely to attend the beginning of the incineration. Heat the dishes thus charged in a muffle at a low red heat, until all organic matter and uncombined carbon have been burned. Cool and weigh.

If an excessive percentage of ash is found, the percentage of mineral matter contained in the alcoholic extract should be estimated by incineration of the residue obtained after evaporation of this extract. If either the total ash or the ash of the alcoholic extract is high, a qualitative examination should be made.

7. Resistance of Pigments and Dyes to Light and Reagents.— It is necessary in the case of cancelling inks, and important, if not necessary, in the case of many stamping inks, that the pigments and dyes employed in their manufacture be as resistant as possible to means which may be employed for the erasure of marks made by them on paper. Under this heading may be mentioned also the importance of the use of dyes which possess considerable affinity for vegetable fibres. It is not practicable to enumerate the agents which should be employed in experiments to ascertain the resistance of a given dye to erasure, as light, heat, and all of the solvents and reagents known to the chemist are available for the use of persons who might desire them for use in assisting them in making fraudulent erasures.

For the purpose of cancelling postage stamps, it is necessary that the cancelling marks be substantially indelible, because the inks used in printing many of the stamps are very resistant. Stamping inks used for other purposes, however, do not require absolute indelibility.

In making the tests use several layers of blotting paper as a pad, pour on this a small quantity of the ink and distribute carefully; see that all excess has been absorbed by the pad before using the stamp. Make a sufficient number of impressions at one time to suffice for all tests and leave some in reserve. Having made the impressions, arrange them in groups according to the colour and kind of ink, and rank them according to the following scheme:

1. Of highest rank.
2. Very good, but not of the best.
3. Good.

4. Fair.
5. Poor.

Having exposed the impressions to the various reagents, as described hereinafter, each sample is again rated according to the effect of the reagents, as follows:

1. Unaffected.
2. Slightly affected.
3. Much affected.
4. Almost effaced.
5. Effaced.

The wet reagents used are pure water, water with the addition of 10% of strong ammonia (sp. gr. 0.90), pure alcohol (95%), alcohol with the addition of 10% of strong ammonium hydroxide, 2% hydrochloric acid, and N/200 bleaching powder. Expose each impression in a small Erlenmeyer flask to about 50 c.c. of the reagent for 24 hours, noting its appearance at the end of 15 minutes, 1 hour, and 24 hours. Then rinse dry and rate.

For the sunlight test expose impressions under glass for 10 days to direct sun, rating at the end of the third, seventh, and tenth days. The tests with reagents are considered of less use than the other tests, and are not always applied.

RUBBER-STAMP INKS.

1. **Preparation and Care of Sample.**—The precautions given in regard to the care of samples of inks made with an oil base should be observed.

2. **Change of Weight on Exposure to Air.**—This estimation should be conducted in the manner described for the estimation of volatile matter in inks made with an oil base. Rubber-stamp inks, however, gain or lose in weight according to the constituents used in their manufacture and according to atmospheric conditions. A rubber-stamp ink should not, however, undergo very much greater changes in weight when exposed to the air under given conditions than diluted glycerin containing 75% of glycerin and 25% of water by volume.

3. **Penetrating Power.**—This test should be conducted in the manner described for inks made with an oil base.

4. **Sedimentation Test.**—This test should be conducted as de-

scribed for inks made with an oil base, with the exception that the portions of ink should be diluted with water instead of with organic solvents.

5. Estimation of Lampblack and Other Constituents.—A scheme of analysis similar to that described for inks made with an oil base should be employed. Some experiments will be necessary in most cases to ascertain the proper solvent to be used in the case of each sample of ink to be examined. Alcohol, however, will generally be found to be satisfactory for rubber-stamp inks. This test is difficult and can not be carried out without a slight loss. To make the loss as small as possible use a very thick felt of asbestos and make the filtration continuous—never allow the gooch to run empty; if it does run empty, it is generally better to begin all over again.

6. Resistance to Light and Reagents.—The remarks made in regard to the investigation of the resistance of cancellations made with oil inks apply in general to cancelling and other inks for use with rubber stamps.

Materials Used for the Manufacture of Cancelling and other Stamping Inks.

1. Volatility and Penetrating Power.—The methods which have been described above will be found useful in determining the suitability of liquids for use as bases or constituents of bases of cancelling and other stamping inks.

2. Sedimentation Test.—A modification of the sedimentation test described may be employed with good results for the purpose of ascertaining the suitability of lampblack and other pigments for use in the manufacture of cancelling and other stamping inks. The results, of course, are mainly of value for purposes of comparison.

The conditions of the test may be modified to suit the purposes of the investigation and the character of the materials to be compared. The writer has obtained good results in the comparison of lampblacks and other blacks rich in uncombined carbon by the following method, which was so planned that the results might be applied to stamping inks made with either a water-soluble base or an oil base:

Mix 0.5 grm. of the black to be tested in a mortar with dilute glycerin (87.5 c.c. of glycerin diluted with water to 1 litre). Rinse the mixture into a 100 c.c. Nessler cylinder and dilute to the 100 c.c. mark, using the

same dilute glycerin. After having prepared a series of tubes, each containing a portion of one of the blacks to be tested, close each tube with a cork and shake thoroughly each tube successively, performing the operation as quickly as possible in order that the time of settling may be approximately the same in the case of each sample. Allow the cylinders to stand at rest in a place free from jar, and record from time to time the height of the sediment formed by the deposition of the blacks. When submitted to this test, a black which is suitable for the manufacture of a cancelling or stamping ink should occupy a volume of not less than 25 c.c. when the sediment has stopped settling.

3. **Ash, etc.**—Blacks, dyes, and other substances used for the manufacture of cancelling and other stamping inks should be carefully examined to insure the absence of considerable percentages of substances which are not essential to the production of an ink of good quality. It can generally be assumed that the presence of considerable quantities of any substance which does not actually contribute to the desirable qualities of the ink will detract therefrom. Black pigments rich in carbon of high sp. gr., due to the presence of a large percentage of ash, are highly unsuitable for the manufacture of stamping inks. Only the concentrated brands of coal tar dyes should be used, unless the substances with which the less concentrated are diluted have been found to actually contribute to the working qualities of the ink to be produced.

TYPEWRITER RIBBONS.

The methods of testing typewriter ribbons given here are those which have been used in the Bureau of Chemistry, U. S. Department of Agriculture (*Bulletin* 109, Revised).

The important things to be ascertained in a typewriter ribbon are length, width, typefilling, character of record (and of copy if it is a copy ribbon), life of ribbon, and resistance of record and copy to reagents and sunlight.

Length and width are frequently specified and these should be recorded, but the rating should be based entirely on quality.

Typefilling.—Take a sufficiently long section of the ribbon on a suitable typewriter (for wide ribbon use a Remington No. 6 and for a narrow ribbon an Underwood No. 5). Carefully clean the small letter e, and using the standard paper used for ink testing make

records of the small letter e, striking the key with as uniform a stroke as possible. Continue writing the letter e until the loop fills so as to demand cleaning the type, or until 8000 impressions have been made. Ribbons which give 8000 clear impressions are given a maximum rating on typefilling, though the test may be carried as much further as may be desired.[1]

Character of record may be determined by examining the sheets from the typefilling test. Note colour, clearness, whether the ribbon appears over- or under-inked, and the tendency to smear. If the ribbon is a copy ribbon make a press copy of the record and make the same observations on the copy and copied original as on the original record.

Life of Ribbon.—For this test the special machine in figure 8 is used. The machine has ten type, the letters A, E, I, O, U, both capitals and small letters. Each type is mounted on the end of a plunger weighing 60 grm. The plunger is raised by a cam and a uniform blow is obtained by allowing it to fall freely for 1.8 cm. The plungers fall one after another in a manner similar to that on a typewriting machine, except that each type strikes a different part of the ribbon from the other type; but the successive blows from the same type fall

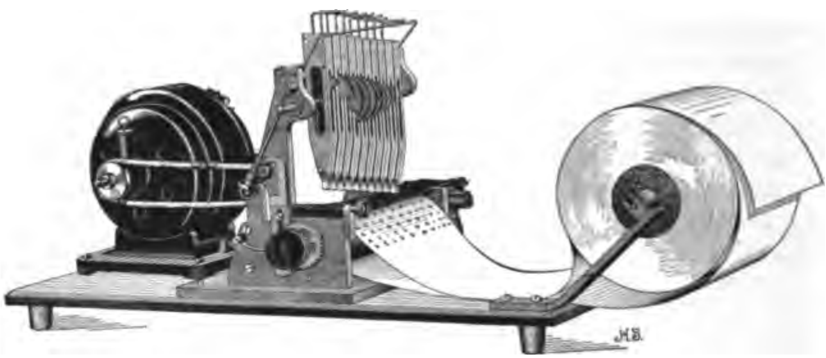


FIG. 6.—Machine for testing life of typewriters' ribbons.

[1] It is exceedingly difficult for an operator to use a uniform stroke in making this test. This makes the comparison rather difficult. In order to avoid this personal equation, since writing the above, the author has had constructed a machine for automatically striking the letter "e". This machine is attached to a standard typewriter, the motive power being a low speed electric motor, which, by a suitable system of gearing, operates a hammer which strikes the letter "e" a perfectly uniform stroke. When the carriage has proceeded to the end of its course, a blank portion of one of the gear wheels causes the operation of the hammer to cease, and at the same time a lever operates a pulley which draws the carriage back and shifts the roll so that the operation is continuous.

on the same spot on the ribbon. The cams are operated by a geared mechanism which is operated from an electric motor connected to the testing machine proper by a belt. When a complete line has been struck, the platen roll is moved forward one space automatically. The ribbon is clamped firmly at one end and the other end passes over a bar and has clamped to it a weight of 45 grm., thus insuring a uniform tension on all ribbons tested. The paper, in strips 14 cm. wide and 41 cm. long (5 1/2 x 16 inches), or fed from a long roll (as shown in the figure), works under the ribbon as in a typewriter. The life of the ribbon is measured by the number of lines of writing which can be made before one or more holes wear in the ribbon, or before one or more type fail to make a clear impression.

Resistance to Sunlight and Reagents.—Cut up the sheets used in determining typefilling and character of record, and subject original, copy, and copied original to the same tests as to resistance to sunlight and reagents that are used on writing inks. Expose to sunlight for at least 14 days, or longer if possible.

Rating.—Length and width are recorded, but are not included in the rating which is based on quality only, the ribbons being marked on a scale of 100.

Typefilling is given a maximum rating of 5 and is marked as follows:

1000 or fewer clear impressions of the small letter e	1
1000 to 3000 clear impressions of the small letter e........	2
3000 to 5000 clear impressions of the small letter e........	3
5000 to 8000 clear impressions of the small letter e........	4
8000 or more clear impressions of the small letter e	5
Character of record is given a maximum rating of	20
Life of ribbon is given a maximum rating of	10
Resistance to reagents is given a maximum rating of	20
Resistance to sunlight is given a maximum rating of	45

CARBON PAPERS.

The practical testing of carbon paper consists in making a carbon copy, using a good quality of medium weight writing paper, such as is used in testing typewriter ribbons, on the special machine used for testing the life of ribbons. The record is examined in the same manner as the ribbon record and is rated as follows:

Character of record is given a maximum rating of	35
Resistance to reagents is given a maximum rating of	20
Resistance to sunlight is given a maximum rating of	45
Total maximum	100

No test need generally be made of the life of a carbon paper, since when struck in the same place all papers are very soon exhausted, no practical difference in this respect having been observed. Of course, in actual use a number of impressions can be made since the type seldom strike in the same place.

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